Experimental Spectroscopy

by

RALPH A. SAWYER, Ph. D.

Professor of Physics
University of Michigan

Preface

The purpose of this book is to discuss prism and grating spectrographs and the techniques of their use in research. It is designed for students of spectroscopy and for those in research laboratories who wish to make use of spectroscopic procedures. For this reason, extensive mathematical treatments have been avoided; a background of general physics and some physical optics should be sufficient for an understanding of the presentation.

The primary emphasis has been placed on those principles and techniques that are fundamental to practically all uses of spectroscopic equipment: the general principles of spectroscopic apparatus, the theory and use of prisms and gratings, photographic procedures, and wavelength and intensity determination have been discussed in extensive practical detail. On the other hand, some related topics and special applications have been discussed more briefly. The treatment of light sources, of spectrochemical analysis, and of infrared and ultraviolet spectroscopy has been supplemented with references to recent and, it is hoped, readily accessible publications. Other more specialized topics which might have been included in such a book as this have been omitted because they have been thoroughly covered in recent texts or because they are of very limited application. In these categories are absorption spectrophotometry and the experimental aspects of the Raman effect and of interferometry, on the one hand, and the Stark and Zeeman effects, on the other. It is believed that readers interested in these topics will desire to consult the more extensive treatments.

References have been made to original sources, and chapter bibliographies have been given of some of the more useful and accessible works on each subject. These bibliographies will make possible the further study of selected topics.

The book was originally planned as a joint undertaking with Dr. H. G. Beutler. Its publication was delayed by Dr. Beutler's unfortunate death in 1942, and its scope necessarily has been somewhat modified by the writer's war duties. Sections 52 and 58–66 are largely the work of Dr. Beutler, and Chapters 3 to 7 benefited much from his criticism.

I am indebted to Professor F. A. Jenkins, of the University of California, for advice on the general plan of the book and for criticism of Chapter 1; to Dean George R. Harrison, of the Massachusetts Institute of Technology, for reading the manuscript; to Lieutenant H. A. Jackson, USNR, who as a student assistant prepared many of the drawings; and, above all, to my wife, Martha G. Sawyer, for invaluable editorial aid.

<div align="right">RALPH A. SAWYER</div>

Contents

CHAPTER 1
History of Spectroscopy

1. Early Ideas on Color

The rainbow must have been one of the earliest external phenomena observed by primitive man. Beautiful and ephemeral, it appealed to his mysticism. He was unable to explain it and was inclined to attribute to it a supernatural significance. Even the most highly developed of the older civilizations, although familiar with simpler instances of refraction, failed to connect them with the rainbow—the spectrum in its natural form. The Alexandrian astronomer, Claudius Ptolemaeus (A.D. 130), in his treatise on optics, described the measurement of angles of incidence and angles of refraction, and later the Arab scientist, Alhazen (A.D. 1038), discussed similar observations. He was aware of atmospheric refraction and of its effect on the apparent position of astronomical objects, but, like the earlier scientists, he failed to discover the law of refraction. Many later scientists, including Kepler, made investigations, but the actual discovery that the sines of the angles of incidence and refraction bear a constant ratio was the work of Willebrord Snell of Leyden (1591–1626).

Snell, like his predecessors, was ignorant of the composite nature of white light and did not distinguish in his measurements the behavior of the different colors. The ancients, and even the best scientists of Snell's time, had but the vaguest ideas concerning the nature of color. Indeed, up to the time of Newton the prevalent ideas seem to have been that white light was changed into different colors within the prism or refracting body, and that color was a mixture of light and darkness. Many of these ideas seem incomprehensible now, but it may be of interest to quote one.

Dr. Isaac Barrow, Newton's predecessor as Lucasian Professor of Mathematics at Cambridge University, as well as his friend and tutor, and the author of a work on optics, *Lectiones Opticae*, must have represented the thought of his time when he described color in this treatise as follows: "White is that which discharges a copious light equally clear in every direction. Black is that which does not emit light at all, or which does it very sparingly. Red is that which emits a light more clear than usual but interrupted by shady intersticies. Blue is that which discharges a rarefied light, as in bodies which consist of white and black particles arranged alternately. Green is nearly allied to blue. Yellow

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is a mixture of much white and a little red; and purple consists of a great deal of blue mixed with a small portion of red. The blue color of the sea arises from the whiteness of the salt it contains, mixed with the blackness of the pure water in which the salt is dissolved; and the blueness of the shadows of bodies, seen at the same time by candle and daylight, arises from the whiteness of the paper mixed with the faint light of blackness of twilight."

2. The Work of Newton

It is a long distance indeed from these strange, inexact notions to our modern theory of the relations between light and color on the one hand, and atomic and molecular structure on the other. The first and longest step in bridging this gap was taken by Sir Isaac Newton (1642–1727). Newton heard Barrow's lectures on optics and was probably familiar with Kepler's *Dioptrice* (1611), in which, by aid of the incorrect assumption that the angle of refraction is proportional to the angle of incidence, Kepler had explained the action of lenses and telescopes. Newton knew also of the first approximately correct explanation of the rainbow, given by Archbishop Antonio de Dominis of Spalato in his *De radiis visus et lucis* (1611), and he had heard of Snell's discovery of the true law of refraction, probably through Descartes' *Dioptrique* (1638). Descartes' own ideas on color were at least explicit. He held that the diversities of color and light were due to the different ways in which matter moves: the various colors were connected with different rotatory velocities of the particles, those which rotate most rapidly giving the sensation of red, the slower ones of yellow, and the slowest of green and blue.

Inspired perhaps by these works, perhaps by his own attempts at lens grinding and the construction of telescopes, Newton, in 1666, at the age of twenty-three, bought a glass prism "to try therewith the phenomena of colors." His experiments, which were simple but fundamental, were described in his first paper in the *Transactions of the Royal Society* in 1672, and in more detail in his *Opticks*, the first edition of which appeared in 1704. He placed red and blue strips of paper side by side and, viewing them through a prism, saw that their apparent displacements were different. Again, he allowed sunlight, entering a round hole in a shutter, to pass through a glass prism and fall on a screen. He recognized that the resulting *spectrum*, as he called it, was a series of colored images of the entrance hole. Further experiments showed him that light once dispersed by a prism is not further dispersed by a second prism, but is merely further refracted. Such light, with rays all alike refrangible, he called *homogeneal*, as distinguished from *heterogeneal* light with rays of different refrangibilities.. He proved that "the Sun's light is a heterogeneous Mixture of Rays," and that in the prism they are "parted or sorted from one another."

Newton understood that the sorting of rays could be carried further and the purity of the spectrum improved by the use of a lens. This he usually placed before the prism and used it to image the entrance hole or slit on the screen. He thus had a spectroscope in nearly modern form, and with it he formed solar spectra as long as ten inches. He apparently failed to see the Fraunhofer lines because of the poor optical quality of his glass—a fault of which he himself complained. Newton realized that different colors must have different indices of refraction and made measurements of the indices of various substances.

Here perhaps Newton's service to spectroscopy ended. An immeasurably great service it was, for his clarification of the nature of color laid the foundation for all later work. In some of his other studies in optics, however, Newton was not so happy or his influence so helpful to progress. He concluded, for example, from his measurements of the index of refraction that dispersion was proportional to deviation for all glasses, that is, that all glasses have the same dispersive powers. Although in his study of telescopes he showed how a combination of lenses could remove spherical aberration, he expressed the opinion that chromatic aberration could not be thus corrected. Newton's prestige was such that this observation certainly retarded the development of better lenses for 150 years. Likewise, he probably delayed the applications of spectroscopy, for in discussing the colors of flames and other lights, he passed from experiment to speculation and proposed that all such lights were of the same nature, were caused by the vibration of the parts of the bodies, and had the same origin as the colors of thin films, which are now explained as arising from interference. As a consequence of this view, Thomas Young (1802) attempted to interpret the yellow line in the spectrum of a candle as an interference effect, and Brewster and Gladstone (1860) used the same explanation for the origin of the Fraunhofer lines. In other words, Newton turned his back on the principle that is the great cornerstone of spectroscopy—the fact that emitted light is characteristic of the atom or molecule that produces it—and nearly 200 years elapsed before this principle was conclusively established.

For a century after Newton, little, if any, progress in spectroscopy was made. In the whole of the eighteenth century the only notable contribution was made by Thomas Melvill, who observed the sodium flame with a prism and published in his *Physical and Literary Essays* (Edinburgh, 1752)[1] the first description of an emission spectrum.

3. Early Nineteenth-Century Developments

The nineteenth century, however, opened with several interesting advances. In 1800 the elder Herschel,[2] British Astronomer Royal,

[1] Reprinted in the *J. Roy. Astron. Soc. Canada*, **8**, 231, 1914.
[2] W. Herschel, *Phil. Trans.*, **90**, 255, 284, 293, 437, 1800.

while studying the distribution of radiant heat from the sun by the aid of sensitive thermometers laid along a solar spectrum, found the radiant heat to be strongest outside the visible red end of the spectrum.   In other words, he discovered the infrared spectrum, although he erroneously believed this radiant heat, which he showed followed Snell's Law, to be something different from light.   The next year, J. W. Ritter,[3] of Jena, studying the effectiveness of the spectrum in blackening silver chloride, found the action to be strongest beyond the visible violet end of the spectrum and thus revealed the existence of the ultraviolet region.

The first wave-length determinations came a year later, in 1802, when Thomas Young brought out his explanation of interference based on the undulatory theory of light, and, taking the measurements of Newton on the colors of thin films, which Newton had been unable to explain by his corpuscular theory, used them to compute the wave lengths of the seven colors recognized by Newton.   The wave lengths were surprisingly accurate and, converted into millimeters, show the spectrum extending from 675×10^{-6} mm to 424×10^{-6} mm.

Also, in 1802,[4] W. H. Wollaston observed the dark lines which interrupt the continuous spectrum of the sun and which are now known as Fraunhofer lines.   His description is not very clear.   He seems to have seen only a few of the stronger of these absorption lines and to have regarded them as natural boundaries of the various pure colors.   Wollaston failed to attach any significance to the lines or to give any explanation of them.   Consequently, his description of them attracted little attention.

In the same paper, Wollaston gave the first descriptions of flame and spark spectra, with no hint as to their fundamental differences for different elements.   In fact, he concluded: "It is needless to describe minute appearances which vary according to the brilliancy of the light, and which I cannot undertake to explain."   In fact, as we shall see, it took a surprising amount of time and effort to show that each element and compound has its own spectrum, and that the light emitted by a luminous vapor gives exact information as to its composition and condition.   Many factors contributed to the difficulties involved—poor apparatus, lack of wave-length standards, impurity of most of the light sources, and incorrect ideas of the causes of color in flames.   For example, Young explained flame colors as interference phenomena arising from the very thin layers into which he believed the droplets in a flame dispersed.

4. Fraunhofer's Discoveries

Although the theoretical development of spectroscopy lagged, its experimental development was more rapid, for a great experimental

[3] J. W. Ritter, *Ann. d. Physik*, **12**, 409, 1803.
[4] W. H. Wollaston, *Phil. Trans.*, **92**, 365, 1802.

genius arose in the person of Joseph Fraunhofer. Born near Munich in 1787, one of a large and poor family, Fraunhofer had little formal education and was apprenticed at the age of eleven to a Munich mirror-maker. He grew with the firm, and his genius was early evident. At 20 he was optical foreman; at 22 a director of the firm; at 24 he was put in charge of the glass making. He made great advances in the development of better machines and techniques for the factory, and when, engaged in experiments to this end, he encountered new phenomena, his genius led him to their full exploitation. Thus began his great interest in pure science.

In 1814, seeking to improve the method of defining the color of light used in measuring the index of refraction of glasses, he made a detailed examination of the spectrum of sunlight. It will be recalled that Newton's spectroscope consisted merely of a slit, a prism, and a lens, which, placed between slit and prism, focused the slit images on a screen. Fraunhofer, to view the slit, used a theodolite telescope placed behind the prism and with it was able to make exact measurements of angles. Placing a 60° flint glass prism 24 feet from a slit in his window shutter, he viewed the light through his theodolite telescope, and found the spectrum crossed with "an almost countless number of strong and weak vertical lines."[5] Experiments with different prisms and slits and other variations of the conditions demonstrated the lines to be really in the sunlight. Fraunhofer could not explain the lines, but he made a map of about 700 of them and assigned to eight of the more prominent ones the letters A to H, by which they are still known. These lines gave him and optical science the first definite standards for the comparison of the dispersion of different glasses, and an exact science of spectroscopy was founded.

Using the first objective prism, a flint glass prism of angle 37°40′ placed before a 4-inch telescope objective, Fraunhofer observed the first stellar spectra. He saw bands in the spectrum of Sirius and lines in those of the planets and other stars. He observed that the planetary spectra were like that of the sun, while those of other stars differed. Fraunhofer was, in fact, the first stellar spectroscopist, and laid the foundations of the science of astrophysics, which has been, and still is, one of the richest contributors to our knowledge of the heavens.

Another great contribution to spectroscopy grew out of Fraunhofer's efforts to improve the manufacture of optical instruments. Studying the behavior of fine slits, he was led to observations on their diffraction patterns. Following the first discovery of diffraction by Grimaldi in 1665, Young, whose work has been mentioned above, and others, had explained the principles of interference. Fraunhofer, however, went on

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[5] *Ann. d. Physik*, **56**, 264, 1817. Some of the original articles by Fraunhofer and by Wollaston are collected in book form under the title *Prismatic and Diffraction Spectra*, translated and edited by J. S. Ames. New York: Harper and Brothers, 1898.

to the case of two, and thence to many, small openings, and discovered the transmission grating. Fraunhofer's first gratings were made by winding fine silver wires upon two fine parallel screws. In this way he made several gratings, using different pitches and wire thicknesses. The finest of these had about 192 lines per centimeter. With such a grating the angle of diffraction for the D lines of sodium in the fourth order is only about 2°30′, yet with this and coarser gratings Fraunhofer made astonishingly accurate wave-length determinations. From ten different gratings he obtained, for the wave length of the D lines, the following values:

.0005891 mm	.0005888 mm
.0005894	.0005885
.0005891	.0005885
.0005897	.0005882
.0005885	.0005882

The average is .0005887 mm, which may be compared with the modern value of .0005892 mm,[6] for the center of intensity of the doublet.

Later, using a diamond point and a ruling machine of his own manufacture, Fraunhofer[7] succeeded in ruling the first glass transmission gratings. With this machine he made two gratings of 3000 and of 625 lines per centimeter, with which he measured the unresolved D lines as .0005886 and .0005890 mm. (The D lines are now known to be a doublet of wave lengths .0005890 mm and .0005896 mm.) These measurements, and others on several other Fraunhofer lines, were the first wave-length measurements of spectral lines and made it possible for results to be quoted in terms of wave lengths rather than in terms of prism angles and telescope settings. Accordingly, greater precision was possible, as well as comparison of the results of different observers. In other words, the stage was set for scientific progress.

Fraunhofer also found time in a busy life for the invention of the heliometer, the eyepiece micrometer, and the achromatic telescope, and to lay the basis of modern optical lens design by trigonometrical computation. These are truly gigantic achievements for one who died at the early age of 39.

5. Characteristic Spectra

One step more remained to put spectroscopy on a scientific basis. The fact that each atom and molecule has its own characteristic spectrum was yet to be recognized. Toward this recognition Fraunhofer made a contribution, for he observed that the yellow lines in a flame were double and seemed identical in wave length with the two dark D lines in the solar

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[6] Fraunhofer's measurements were made in Paris inches. (1 Paris inch = 27.0700 mm.)

[7] J. Fraunhofer, *Ann. d. Physik*, **74**, 337, 1823.

spectrum. Nevertheless, these D lines, which we now know to be due to the sodium atom, formed one of the great stumblingblocks to the final clearing up of this point. For sodium is one of the most common of contaminations. It is always present on the hands from perspiration, and it is found in most vegetable and animal matter. It is hard, indeed, to observe an arc or flame spectrum which is free from sodium lines. Calcium lines likewise are usually present in arc or flame spectra, and lines due to the oxygen and nitrogen of the air appear in practically all spark spectra.

These similarities, as well as other supposed similarities actually due to poor measurements, misled observers for many years after Fraunhofer, although numerous investigators were on the verge of discovering that each atom and molecule has a characteristic spectrum. Later numerous unfortunate *post hoc* controversies raged over priority of the discovery, since none of the claimants had made an unequivocal statement in his analysis of his observations.

The younger Herschel, J. F. W. Herschel, son of the discoverer of the infrared spectrum, made extensive studies of the flame spectra of salts.[8] He described the different colors imparted to flames by the salts of various metals, and said, "The colours thus communicated by the different bases to flames afford, in many cases, a ready and neat way of detecting extremely minute quantities of them." This statement would seem unequivocal, had he not qualified it by observing, "When the combustion is violent, as in the case of an oil lamp urged by a blow pipe, or in the upper part of the flame of a spirit flame, or when sulphur is thrown into a white hot crucible, a very large quantity of a definite and purely homogeneous light is produced." Here two or three yellow radiations are confused. Nevertheless, Herschel seems to have been near the truth; he recognized that some substances give definite spectra but not that one spectrum can belong to one, and only one, substance.

Another English observer of flame and spark spectra was W. H. Fox Talbot, who in 1825 said, in describing flame spectra,[9] "The orange ray may be the effect of the strontia, since Mr. Herschel found in the flame of muriate of strontia a ray of that colour. If this opinion should be correct and applicable to other rays, a glance at the prismatic spectrum of a flame may show it to contain substances which it would otherwise require a laborious chemical analysis to detect." Ten years later he reiterated that lithium and strontium could be distinguished spectroscopically, and described other spectra, but he seems never to have been entirely clear as to the significance of characteristic spectra.

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[8] *Encyclopedia Metropolitana*, Volume IV, "Light." London: B. Fellowes, 1817–1845.

[9] W. H. Fox Talbot, *Brewster's J. Science*, 1825, p. 77.

Many others during the first half of the nineteenth century observe and described various flame and arc spectra; it is beyond our scope t describe their work in detail.   Among them were Sir Charles Wheatston(the English physicist, whose work on metallic sparks, briefly reported t the British Association for the Advancement of Science in 1835, wa published in full in 1861 by Sir William Crookes.   Wheatstone seems t have understood that the spectra came from the volatilized particle which entered the flames and that the different metals were charac terized by different and distinctive spectral lines, but he failed to recog nize the significance of this discovery.   The Swedish physicist, Ångström in 1855, and the American physician, Alter, in 1854–1855, publishe(descriptions of metallic spectra and, like Wheatstone, again noted th characteristic differences in different spectra.   Ångström also describe(gaseous and absorption spectra.   The French physicist, Foucault, i1 1848 observed that a sodium flame which emitted the D lines of sodiun would absorb these very rays from the stronger light of an arc place(behind it.   It is clear from these examples that many workers ha(observed some of the facts of characteristic emission and absorption an(noted some specific relationships and peculiarities.

6. Kirchhoff and Spectrum Analysis

It remained, however, for another scientific giant, Kirchhoff, t(point out the general law connecting absorption and emission of light and to emphasize the great significance of the characteristic spectr: emitted by different elements.   Kirchhoff, who was Professor of Physic: at Heidelberg, in 1859 announced his law and its mathematical proof and pointed out applications in two papers before the Berlin Academy ol Science.[10]   Kirchhoff's Law states: "The relation between the powers ol emission and the powers of absorption for rays of the same wave length i: constant for all bodies at the same temperature."   Thus, a transparent body cannot emit light and one which radiates a continuous spectrum must be opaque.   Or, further, a gas which radiates a line spectrum must absorb the lines which it radiates at the same temperature.   Kirchhofl showed, by passing sunlight through a gas flame containing common salt, that the yellow lines of sodium were identical with the Fraunhofer D lines, and, furthermore, that this same sodium flame would absorb this same yellow light from a stronger light behind it.   He went on to explain the dark Fraunhofer lines in the solar spectrum as caused by the absorption by the elements in the cooler sun's atmosphere of the continuous spectrum emitted by the hot interior of the sun, and observed that sodium and calcium were certainly present, while lithium appeared to be absent.

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[10] G. R. Kirchhoff, *Monats ber. d. Ber. Akad. d. Wiss.*, 1859, pp. 783–787; *Ann. d. Physik*, **109**, 148, 275, 1860; *Phil. Mag.*, **20**, 1, 1860; *Ann. Chim. Physique*, **58**, 254, 1860.

The way was thus opened for the chemical analysis of the sun's atmosphere, and Kirchhoff, in conjunction with the Heidelberg Professor of Chemistry, R. Bunsen, immediately attacked the problem. They examined the flame and spark spectra of the purest elements available and were able to demonstrate the presence of a number of metals in the sun. In the progress of the research, Kirchhoff was led to make a very complete map of the solar spectrum and of the spectra of many of the metallic elements. Unfortunately, the lines were located not by their wave length, but in terms of the micrometer scale of the spectrometer used, and they were, accordingly, not useful as standards.

Kirchhoff and Bunsen[11] also applied themselves to the problem of chemical analysis with the spectrometer. In the course of their study of the alkali metals, they discovered, in 1861, a fourth alkali metal, caesium, and later in the same year still a fifth one, rubidium. They were soon able to isolate these new elements and describe their properties.

The demonstration by Kirchhoff and Bunsen of the power of the spectrometer may certainly be said to have founded modern spectroscopy. Scientists in all countries were stimulated to undertake spectroscopic investigation, and great popular interest was aroused. It has, in fact, been said that the discoveries of Kirchhoff and Bunsen gave as great a stimulus to popular interest in science as the relativity theory of Einstein was to provide half a century later.

Unfortunately, controversies arose as various scientists claimed for themselves or for their fellow countrymen that earlier spectroscopic researches gave them a priority over Kirchhoff in the discovery of the principle of spectrum analysis—that spectra are characteristic of the atoms and molecules that produce them—or in the enunciation of Kirchhoff's Law of Emission and Absorption. Kirchhoff's own position is tolerantly and clearly stated in a paper, "On the History of Spectrum Analysis."[12] There seems no doubt that while others, as was pointed out above, may have been near the truth or parts of it, it was Kirchhoff who had the vision and ability to state the general laws so clearly and convincingly as to attract the attention of the scientific world.

7. Standard Wave Lengths

The great volume of work which followed on flame, arc, and spark spectra, solar and stellar spectra, and their variations and modifications cannot be discussed in detail. The weakness of all this work was a common lack of accuracy and of suitable standards of wave length. The first useful standards were provided by Ångström, in 1868, in his great research on the sun spectrum. In his *Normal Solar Spectrum* he gave a

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[11] G. R. Kirchhoff and R. Bunsen, *Ann. d. Physik*, **110**, 160, 1860; *Phil. Mag.*, **20**, 89, 1860, and **22**, 329, 1861; *Ann. Chim. Physique*, **62**, 452, 1861.

[12] G. R. Kirchhoff, *Phil. Mag.*, **25**, 250, 1863.

chart with wave lengths of about one thousand of the Fraunhofer lines. The wave lengths were determined from grating spectra by interpolation between nine of the strongest lines, whose absolute wave lengths had been carefully determined by measurements on three glass gratings ruled by Norbert.   The wave lengths were given to six significant figures and were expressed in terms of ten-millionths of a millimeter, or 10^{-8} cm—a unit which has since been known as the angstrom unit, abbreviated as Å or AU, and used as a unit for all spectroscopic measurements.

Ångström's work was widely accepted as standard, and other measurements were given in terms of these solar wave lengths.   Ångström's wave lengths, however, were based on his measurement of the grating space of his glass gratings, in terms of the Upsala standard meter.   Unfortunately, as was discovered later and announced by Thalén in 1884, the length of the Upsala meter was not 999.81 mm, the value used by Ångström, but 999.94 mm.   Accordingly, the wave lengths were all too small by 13 parts in 100,000.

Numerous attempts were made in the next few years to provide better standard wave lengths.   The earlier work had all been done visually, but with the development of the dry gelatine photographic plate about 1870, photographic methods, with consequent improved accuracy, began to be used.   At the same time, Professor Henry Rowland, of Johns Hopkins University, not only began to produce far better gratings than had previously been made, but also invented the concave grating, which permitted the much more accurate comparisons of wave length achieved through the coincidence method.   In 1887 Rowland[13] was able to publish new lists of solar wave lengths, and in the following years wave-length tables both of the arc spectra of many of the elements and of the Fraunhofer lines.   These tables were accepted as standards for the next twenty years.   Most of the spectroscopic publications of the period give their results in Rowland units—that is, in angstrom units based on Rowland's standards.

Rowland based his tables upon the weighted mean of the best available determinations of the wave length of D_1, the longer wave-length member of the two yellow sodium lines.   He averaged them as follows:

Weight	Observer	D_1
1	Ångström, corrected by Thalén (1884).....................	5895.81
2	Müller and Kempf (1886)...............................	5896.25
2	Kurlbaum (1888).......................................	5895.90
5	Peirce (1879), corrected by Bell........................	5896.20
10	Bell (1887)..	5896.20
	Weighted mean..	5896.156

[13] H. A. Rowland, *Phil. Mag.*, **23**, 257, 1887; *Am. J. Sci.*, **33**, 182, 1887.

Rowland's wave lengths covered the range from 2152.91 to 7714.68, and he believed them to be accurate to .01A and so consistent that any later correction in the value of D_1 could cause only a proportional error in the whole list.

Rowland's belief in the relative accuracy of the standard wave lengths unfortunately turned out to be unjustified. In 1893, by the use of an interferometer, Professor A. A. Michelson,[14] of the University of Chicago, was able to measure the wave lengths of three cadmium lines in terms of the standard meter at Paris and attained an accuracy far exceeding that of any previous work. Michelson's values are compared with Rowland's in the following table:

CADMIUM WAVE LENGTHS

Line	Michelson	Rowland	Ratio
Red Cadmium................	6438.4722×10^{-8} cm.	6438.680	1.000033
Green......................	5085.8240	5086.001	1.000036
Blue.......................	4799.9107	4800.097	1.000039

It is obvious that the two sets of values are not consistent, since they do not have a constant ratio. Michelson found that the D_1 line of sodium (5895.932A, in terms of his cadmium values) was not sufficiently sharp and homogeneous for use as a standard.

In 1900 Fabry and Perot at Paris extended the interferometer method to lines of other elements, determining their wave lengths in terms of Michelson's value. It became increasingly apparent that Rowland's standards were not only absolutely, but also relatively, in error. The newly formed International Union for Co-operation in Solar Research, meeting at St. Louis in 1904, took up the question of suitable standards. Meeting at Oxford in 1905, it agreed to adopt a suitable spectroscopic line as the primary standard and to determine secondary standards by interferometric comparison with this primary standard. At Meudon, in 1907, the red cadmium line as emitted under specified conditions in dry air was adopted as the primary standard, and Fabry, Perot, and Benoit's value of 6438.4696A was accepted[15]—Benoit's correction of Michelson's value, to dry air at 15°C and 760 mm of mercury pressure, gave 6438.4695. At later meetings of this Union and of the International Astronomical Union, which, in 1922, succeeded to the work that had been interrupted by the war, numerous secondary standards in the arc spectrum of iron and in rare-gas spectra were adopted. These lines have all

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[14] A. A. Michelson, *Phil. Mag.*, **24**, 463, 1887; **31**, 338, 1891; **34**, 280, 1892.

[15] Wave lengths based on the primary standard are abbreviated A to distinguish them from wave lengths based on older standards and abbreviated Å.

been measured by two or more observers and may be relied on as accurate to about .001A.   Wave-length determinations, however, are now being made interferometrically that are accurate to a few ten-thousandths of an angstrom unit.

As has been stated, the early spectroscopic observations were all made visually and so were limited to the wave-length range of the sensitivity of the eye.   This range varies somewhat with individuals, but is roughly from 4000 to 7500A, although young observers, when all visible light is excluded, are able to see much shorter wave lengths, even to 2000A, in the ultraviolet as a bluish sensation.[16]

8. The Ultraviolet and the Infrared

The first noteworthy extension of the ultraviolet spectrum was made in England by G. G. Stokes,[17] who, in 1862, discovered the transparency of quartz in this region and, with the help of a uranium phosphate fluorescent screen, observed the arc and spark spectra of numerous metals. Although he could make no wave-length determinations, he appears to have seen the aluminum doublet at 1858, 1862A.   The first wave-length determinations in this region were made a year later, in 1863, in France, by Mascart, who photographed the ultraviolet solar spectrum, which ends at about 2950A, and made measurements, although of no great accuracy.   Accurate ultraviolet measurements, as noted above, were first provided by Rowland, whose work extended to 2150A.   Further extension of the ultraviolet by ordinary means is prevented by the absorption of the photographic gelatin, which rapidly reduces the emulsion sensitivity for wave lengths shorter than about 2300A, and by the absorption of the oxygen in the air, which sets in strongly at about 1850A.   By making photographic plates almost free from gelatin, by substituting for quartz prisms and lenses, optics made of fluorite, and by enclosing the whole equipment in an evacuated chamber to eliminate the absorption of the oxygen, Victor Schumann[18] succeeded in extending the ultraviolet spectrum to 1200A.   This limit was set by the absorption of the fluorite. A great extension of the ultraviolet limit was achieved in 1906 by Theodore Lyman, who substituted the concave grating for the fluorite optics. The only losses in the system, then, were those due to the reflection at the grating surface.   With this equipment Lyman made wave-length measurements down to 500A.   Later improvements in light sources, grating ruling, and mounting by Millikan, Bowen, and Sawyer and by Siegbahn and his associates have progressively reduced this limit to below 30A—a limit which has now been reached from the short wave-length side by

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[16] J. Saidman, *Comp. Rend.*, **196**, 1537, 1933.

[17] G. G. Stokes, *Phil. Trans.*, **152**, 599, 1862.

[18] V. Schumann, *Wien. Sitzber.*, **102**, 415, 625, 994, 1893.

X-ray spectroscopy. Some of the special techniques used in this extreme ultraviolet region will be discussed in Chap. 12.

Rowland's measurements at the red end of the spectrum ceased at 7715A, the limit of sensitivity of the usual red-sensitive photographic emulsion. Abney had shown, in 1880, that it was possible by a very difficult technique to prepare photographic plates sensitive to about 20,000A. Few have been able to duplicate his technique, but photographic plates are now available commercially which are sensitive to about 12,500A. The big extensions of the infrared region of the spectrum have been made by non-photographic, physical devices which are sensitive to radiant energy. Professor S. P. Langley, of Washington, D. C., in 1881, devised the bolometer, a very sensitive electrical resistance thermometer, by means of which, in this and succeeding years, he was able to extend the solar spectrum to 180,000A. In the years from 1892 on, tremendous advances were made in Germany by Rubens and by Paschen, who, together with their pupils, were very active in all phases of infrared research. As a result of their work, and that of others, with various techniques and equipment, some of which will be described later, the radiation spectrum has been investigated far into the infrared, to wave lengths of about 3,000,000A, or .3 mm—a region which, in fact, overlaps the shortest radio waves.

9. Recent Developments

Very interesting data on the growth of interest in spectroscopy have been presented by the late Professor Kayser, of Bonn,[19] in a statistical study of his remarkably complete collection of publications of spectroscopic researches from all countries. He has classified the papers by country, as well as by year, but for our purpose a graph representative of the total number of papers is perhaps most instructive. Fig. 1 (page 14) shows the average numbers of spectroscopic researches published per year during each of the five-year periods (1800 to 1915) which begin with the year plotted. Two periods of very rapid growth in interest in spectroscopy are strikingly apparent. The steep rise from 1855 to 1865 indicates the tremendous stimulus to spectroscopic work given by the publication of Kirchhoff's classic papers in 1859 and of the work of Kirchhoff and Bunsen beginning in 1860. The second great impetus to spectroscopic research began in 1885 following the discovery by J. J. Balmer[20] that the wave lengths of the hydrogen lines could be represented by a simple mathematical formula. Beginning in 1890, Kayser and Runge[21] at Bonn, and the Swedish physicist, Rydberg,[22] extended this

[19] H. Kayser, *Phys. Zeits.*, **39**, 466, 1938.
[20] J. J. Balmer, *Ann. d. Physik*, **25**, 80, 1885.
[21] H. Kayser and C. Runge, *Abh. d. Berl. Akad. d. Wiss.*, 1890–1893.
[22] J. R. Rydberg, *Comp. Rends.*, **110**, 394, 1890.

idea to the arrangement of the lines of other elements in series following simple laws.

The interest in the earlier period was largely concerned with the chemical and physical properties of matter as revealed by the spectrograph, and with the astrophysical applications of the spectrograph; in the second period it was the power of the spectrograph in revealing the secrets of atomic structure that stimulated new interest in its use. New discoveries in the use of spectrographic data in the interpretation of the
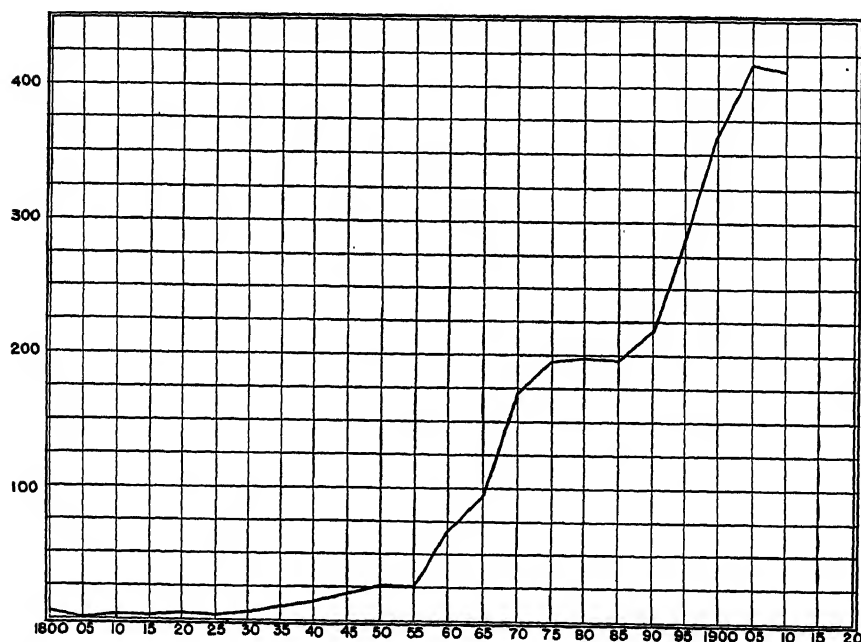
Fig. 1. Number of Spectroscopic Research Papers Published in Each of the Five-Year Periods from 1800 to 1915.

properties of atoms and molecules kept this interest active well into the twentieth century. The whole period from 1860 almost to the present has been rich in such fundamental discoveries, each opening new fields of spectrographic research and leading to the enlargement and refinement of our understanding of the atom and of its mathematical theory. It is impossible to discuss all of these steps; some of them, however, should be mentioned. Among the outstanding pieces of work of the last half century are Zeeman's discovery of the magnetic splitting of spectral lines (1896); the studies of fluorescence begun by Stokes and leading to Wood's discovery and study in the early years of the century of the resonance radiation of vapors; the Bohr theory of the hydrogen atom

(1913), which initiated a period of tremendous development of atomic theory, with its extension by Sommerfeld and others, culminating in quantum mechanics and the wave theory of the atom of Schrödinger and DeBroglie (1925–1926); the first analysis of the complex spectra of atoms in the higher columns of the periodic table by Catalan in 1926; and the spectroscopic determination of nuclear spin by Goudsmit and
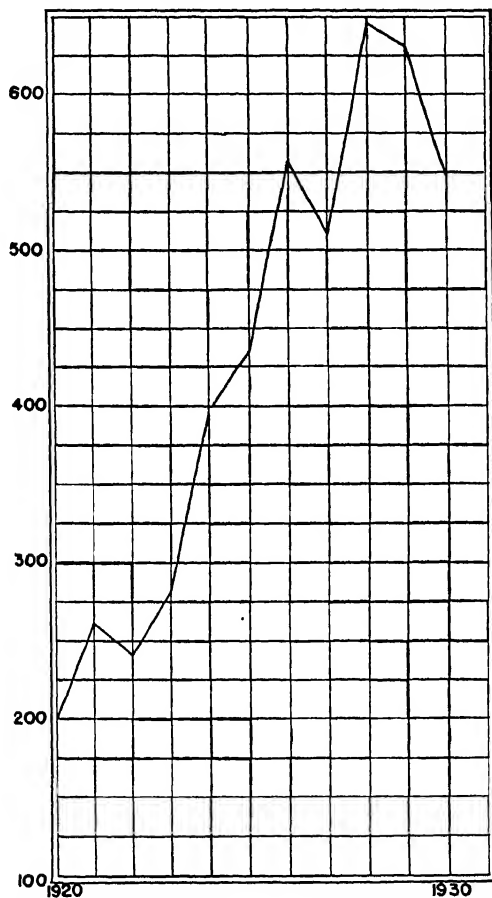
Fig. 2.   Number of Research Papers on Line Spectra Published in Each of the Years
from 1920 to 1930.

Back (1926).   Many others could be cited, all of which contributed to the field of spectrographic research.

The extent of the interest in spectroscopy in the postwar period is shown by Professor Kayser's data for the years 1920–1930, which are represented graphically in Fig. 2.   This graph is not exactly comparable with Fig. 1, since data are shown by individual years rather than by five-year periods, and since researches on astrophysics, absorption, and other

phases of spectroscopy, which were included there, are here omitted, and only work on the line spectra of atoms and molecules is included. In the early years is shown the recovery from the interruption of research by the war. In the later years the decline in the number of papers reflects the approaching exhaustion of the field of classification of spectra and associated problems.

In other fields of research, however, a consideration of the extent of the utilization of the spectrograph would probably reveal that actually spectrographic methods and equipment are in greater use than ever before. In the field of pure research, new uses for the spectrograph seem virtually inexhaustible. In astronomy, the spectrograph, the spectro-heliograph, and the new spectroheliokinematograph are among the essential instruments. In the physics laboratory, many problems involving discharge phenomena and reactions and elementary processes in electrical discharges are attacked with the aid of the spectrograph. The study and analysis of the spectra of polyatomic molecules have attracted more and more interest in recent years in both physics and chemistry laboratories. Spectroscopic methods have also been found to be powerful tools in the investigation of photosynthesis and the study of chemical reactions.

In applied science, never sharply and completely separated from pure science, the use of the spectrograph has been rapidly increasing. An important case is the rapid and precise chemical analysis by the spectrograph, a process that is known as *spectrography* or *spectrochemical analysis* and that finds application in almost any situation where chemical analysis by wet methods is used. An indication of interest in such process is found in the *Index to the Literature in Spectrochemical Analysis* by Meggers and Scribner.[23] Here are listed for the period 1920–1937 all the papers in the field known to the authors. As will be seen from the following tabulation, recent years have seen a remarkable extension of the work in this field.

PUBLICATIONS ON SPECTROCHEMICAL ANALYSIS

Year	Number	Year	Number	Year	Number
1920	5	1926	23	1932	70
1921	12	1927	30	1933	91
1922	9	1928	31	1934	113
1923	18	1929	42	1935	128
1924	9	1930	46	1936	121
1925	10	1931	64	1937	118

[23] W. F. Meggers and B. F. Scribner, *Index to the Literature in Spectrochemical Analysis*. Philadelphia: American Society for Testing Materials, 1939.

An attempt has been made in the preceding pages to give a sketch of the outstanding steps in the development of spectroscopy.   Much detail and much important work have necessarily been omitted.   For a complete discussion of the historical development of spectroscopy, some of the more detailed and extensive texts should be consulted.

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Kayser, H., *Handbuch der Spectroscopie*, Vol. I, especially Ch. I. Leipzig: S. Hirzel, 1900.   This standard work gives a very complete treatment of the subject up to the time of its publication.

More, L. T., *Isaac Newton*.   New York: Charles Scribner's Sons, 1934.

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Encyclopaedia Britannica, 11th ed., Cambridge University Press, 1910, and 14th ed., Encyclopaedia Britannica Company, London, 1936.   Numerous useful articles will be found under the title "Spectroscopy" and also under the names of particular individuals.

CHAPTER 2
Light Sources

Practically all the artificial light sources known to man have been studied spectroscopically, as have also the radiations from all the luminous celestial bodies. The spectrograph is a powerful tool for the investigation of the nature and properties of any source and for the study of the composition and character of the material emitting the radiation. The information that can be gained by use of the spectrograph depends to a considerable extent on the proper choice and use of the available light sources.

A detailed discussion of all available light sources cannot be undertaken here. For that, the various special publications on the subject must be consulted. However, some of the general features of spectroscopic light sources and some details of their behavior will be presented.

Light sources are classified, according to the spectrum they emit, as continuous or discontinuous. A continuous spectrum is characterized by a generally uninterrupted range of wave lengths over a considerable region, and by the absence of sharp lines or bands. In the visible region this spectrum appears as an unbroken series of colors changing imperceptibly from one to the next. Discontinuous sources, on the other hand, show a number of sharp, narrow "bright lines" in their spectrum. The radiation is emitted by the individual atoms or molecules in the light source, which are usually in a vapor or gaseous state.

The distinctions between the two types of spectra are not absolutely sharp.

10. Continuous Sources

Continuous spectra are characteristic of incandescent solids and liquids, such as lamp filaments; of certain high-pressure discharges, such as underwater sparks or violent condensed discharges in narrow capillaries; and of certain gaseous discharges, such as the uncondensed discharge in hydrogen in which a continuum may be excited. The particular source to be chosen depends on the purpose for which it is to be used and particularly on the wave-length region to be covered.

Simple incandescent bodies, such as black-body radiators and incandescent filaments, which approximate black bodies, emit a continuous spectrum, the distribution of which is fixed solely by the temperature of the emitting solid, according to the well-known Planck Distribution Law

(Fig. 3). At ordinarily attainable temperatures, such hot solids are most useful as sources in the visible and near-infrared regions, since their spectra reach their maximum in the near-infrared and fall off rather rapidly on the red side and more gradually toward the violet. They are commonly used for studies in these regions because of their convenience and simplicity.

For a continuous source in the infrared, it is more common to use some incandescent substance which combines with general black-body radi-
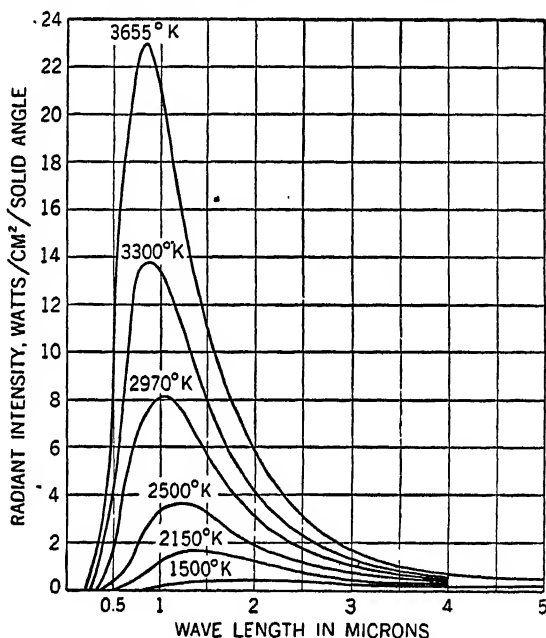
Fig. 3. Spectral Distribution of Black-Body Radiation for Several Temperatures according to Planck's Law.

ation a high selective emissivity in the desired region. A great advantage of such selective radiators is the weakness or absence of unwanted radiations, which can be a great source of trouble by contaminating the desired spectral regions with scattered radiation or with spectra of overlapped orders. Examples of selective radiators are the Welsbach mantle, which emits strongly in the visible and in the infrared beyond 8μ but only weakly in the near-infrared, and the globar heater, which emits strongly beyond 20μ. An interesting case is that of powdered crystals of various materials which, as Pfund has shown,[1] may be chosen so as to have, when heated, bands of selective emission in special regions which are determined by the selective absorption of the particular material used. Thus,

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[1] A. H. Pfund, *J. Opt. Soc. Am.*, **23**, 270, 1933.

quartz has emission bands near 8.50μ, 9.02μ, and 20.75μ, while the bands of fluorspar are at 24.0μ and 31.6μ, and of sodium bromide at 50–55μ.

For continuous sources in the ultraviolet, some type of discharge must be employed. One which has been much used is the underwater spark. If a vigorous condensed spark is operated between electrodes of any high-melting-point metal under flowing distilled water, a strong continuous spectrum is radiated which extends well below 2000A.[2] This source is not very uniform in intensity nor very steady in operation. When a more controllable source is desired, many observers have favored an uncondensed discharge at perhaps 1000 volts 60 cycle a-c in a large H-type discharge tube containing hydrogen at from 1 to 2 millimeters pressure. When a "capillary," 1 centimeter or so in diameter and 20 or 30 centimeters long, is immersed in flowing cold water and viewed end-on, a current strength of a few amperes produces a continuous spectrum of high intensity and uniformity extending from about 3500A to near 1200A in the extreme ultraviolet. Details of the construction of such tubes have been given by various workers.[3]

For the extreme vacuum-ultraviolet region, the most satisfactory continuous source is the strong current discharge in hydrogen or helium. In helium, this discharge is useful between 900A and 600A and nearly, if not quite, overlaps the continuum of hydrogen.[4]

11. Line Sources

Discontinuous spectra, almost without exception, are radiated from atoms or molecules in a gaseous or vapor state which have stored up excess energy in some manner and then radiate it as luminous energy. Sources differ in the method by which energy is supplied to the atoms and in the amount which can be absorbed before radiation. Atoms or molecules may receive energy by absorption of radiation, as kinetic energy from collisions with electrons or atoms, by taking energy excitation from other atoms or molecules which have absorbed energy, or by thermal excitation, which is usually a combination of the other types.

Simple thermal excitation is found in flame spectra and furnace spectra. The actual processes involved in these cases are, no doubt, a mixture of the other modes of excitation, the energy which the colliding electrons, atoms, or molecules possess being provided by the kinetic energy of thermal agitation. The actual temperatures attained in furnaces or flames are relatively low. Since the energy given to atoms or molecules is correlated directly with the temperature, the spectra emitted by these sources are made up largely of "low temperature"

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[2] Cf., for example, H. S. McNicholas, *Bur. of Stand. J.*, **1**, 939, 1928.
[3] E. O. Lawrence and N. E. Edlefsen, *Rev. Sci. Inst.*, **1**, 45, 1930.
[4] J. J. Hopfield, *Astrophys. J.*, **72**, 139, 1930.

or "arc" lines—characteristic of atoms or molecules in low stages of excitation.

These simple sources have the advantages, especially in the case of the furnaces, of producing a simple spectrum with satisfactory uniformity and controllability. They have been used for investigation of the processes of excitation and, as an aid in the analysis of complicated spectra, for study of atomic spectra at successive stages of excitation. Lundegårdh[5] has recently used the flame for quantitative spectroscopic analysis. He used a form of atomizer to spray solutions of the materials to be investigated into an oxyacetylene flame. The steadiness and simplicity of this source recommend it for cases where the use of solutions is convenient or desirable.

12. Electric Arcs

An electric arc between two solid electrodes is a simple and popular source. No equipment is required except an insulating holder for the electrodes, a direct-current source of 100 or more volts, and a ballast resistance. The ballast resistance is necessary because the voltage across an arc depends almost wholly on the nature of the electrodes, the pressure and character of the surrounding gas, and the length of the arc, and very little on the current. The voltage-current characteristic is very steep and may even have a negative slope in some regions, so that, without a ballast resistance, the current is unstable and may increase without limit until a fuse or circuit burns out.

The excitation of the atoms and molecules, at least in the arc column when not too close to the electrodes, is approximately pure thermal, with an equivalent mean temperature of 3500–8000°C. Because of these higher temperatures, the spectrum contains, in addition to the lines or bands found in flame spectra, many new lines which require more excitation. Except in the case of the more easily ionized atoms, they are still, however, predominantly the lines emitted by the neutral atom. In the regions close to the electrodes, the excitation is higher and lines of ionized atoms are often found.

Arcs are sometimes operated in another atmosphere, such as nitrogen, hydrogen, helium, or argon.[6] The arc in most of these gases gives a higher "temperature" or excitation than does the arc in air. Arcs may also be operated at reduced pressures, which tend to produce lines that are of much higher excitation as well as sharper and free from the small line displacements caused by pressure effects.

The arc has many advantages as a spectroscopic source. It is cheap and simple to set up and can be used with any kind of conducting elec-

[5] H. Lundegårdh, *Zeits. f. Physik*, **66**, 109, 1930.

[6] F. Paschen, *Ann. d. Physik*, **12**, 509, 1932.

trodes. Very small amounts of impurities in pure electrodes are readily detectable. Scarce materials, nonconducting elements, or salts can be packed in holes drilled in the tips of graphite electrodes; solutions can be dried on the tips of graphite or copper electrodes. However, for work in which uniform relative intensities of the spectral lines are important, the d-c arc does not give as constant and reproducible results as some other sources. The variability arises, to a considerable extent, from wandering of the cathode "spot." This spot, small and intensely hot, is the seat of most of the electron emission which maintains the discharge. It is inclined to wander irregularly from one point to some other which, for reasons not wholly understood, is at the moment a preferred emitter. Resultant large and inverse fluctuations of current and voltage accompany this wandering. A concomitant effect is fluctuation of the discharge temperature, which, in turn, causes variations in the relative intensities of the lines.

The wandering of the disengaging area on the electrode leads to variations in the rate of evaporation of material from the electrode. If several elements are present in the electrode, their relative rates of evaporation will vary in a manner dependent on their different boiling points. Further results of these different fluctuations are variations in the volume and density of the arc discharge, which, together with the temperature fluctuations, lead to variable self-reversal in the lines emitted by the arc.

Some of the irregularities in the behavior of the direct-current arc may be avoided by the use of the high-voltage alternating-current arc introduced by Duffendack and Thompson for quantitative spectrochemical work.[7] In this discharge, 1,000 or more volts at 60 cycles from a transformer are connected through a large ballast resistance or inductance across an electrode gap of only two or three millimeters. The arc may be started by closing the gap, or the applied voltage may be high enough for an initiating spark to render the gap conducting. Once the gap is ionized, the discharge continues as an arc with a constant voltage fixed, as in the d-c arc, by gap conditions, and with a sinusoidal current fixed by the transformer voltage and the ballast. The arc is extinguished when the gap voltage falls below the sustaining voltage, and strikes once more as the transformer voltage rises again with the opposite polarity. The reignition of the arc, twice per cycle, and usually to a new cathode point, eliminates many of the troubles caused by the erratic wandering of the cathode spot in the d-c arc. The a-c arc, though more complicated than the d-c arc to set up, gives more uniform and reproducible relative line intensities and has been widely used for quantitative spectrochemical analysis.

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[7] O. S. Duffendack and K. B. Thompson, *Proc. Am. Soc. Testing Materials*, **36**, II, 310, 1936.

13. The Electric Spark

For a source with higher excitation and one which is more flexible in power and control, the spark in its numerous modifications has many applications. In all modern forms, the spark is produced by connecting the secondary of a transformer giving from 10,000 to 50,000 volts across an insulated electrode-holder which carries the test samples. In most cases a condenser is connected in parallel across the secondary, also. The effect of the condenser is to increase greatly the discharge current across the gap. The condenser is charged on every half-cycle to the voltage at which the gap breaks down. An oscillating discharge current then flows in the spark circuit with an initial value (if the ohmic resistance of this circuit is negligible) given by

$$I = V \sqrt{\frac{C}{L}}$$

where V is the condenser voltage at the time of discharge, C the capacity in farads, and L the circuit inductance in henries. The initial current may easily be hundreds of amperes. The result is an almost explosive emission of excited vaporized material from the electrodes. The high-frequency, alternating current may, and in fact should, be damped rapidly so that the spark gap may become nonconducting before the next half-cycle, thus permitting the voltage to build up again on the condenser in time to repeat the discharge train.[8]

The transformer must have a size adequate to charge the condenser, otherwise the condenser will not reach the expected voltage. Since the current drawn by a condenser is given by $I = 2\pi n C V$ (n being the frequency of the alternating voltage supply), the power demand is $W = VI = 2\pi n C^2 V$. This calculation does not take into account any power drawn by the spark discharge. The condenser may be of almost any size, from a few thousandths up to a few tenths of a microfarad. The larger the condenser, the larger the initial current and the rate of energy dissipation in the spark gap and, in general, the higher the excitation of the atoms of the electrode material. Spark discharges in most cases have higher equivalent temperatures than do arcs. The effective temperature of a spark discharge, and hence the excitation produced, increases with increasing voltage or condenser capacity, since these increase the current density of the discharge. In the most vigorous sparks, the apparent temperature may be as high as 10,000°C.

A small amount of inductance is desirable in the spark circuit, since it has been found to prevent the excitation of lines and bands of the air

[8] A good discussion of the phenomena of spark discharges is given by H. Kaiser and A. Wallraff, *Ann. d. Physik*, **34**, 297, 1939.

molecules which otherwise cause undesirable confusion and background in the spectrum. Larger amounts of inductance decrease the initial current and degree of excitation in the spark. In fact, Fowler[9] has used the variation of inductance as an aid in separating the spectral lines from the various stages of ionization of the silicon atom.

With an applied voltage of the order of 50,000 volts and a spark gap of about one millimeter, the spark discharge will operate in the highest attainable vacuum. This "vacuum spark" was applied by Millikan and Sawyer[10] to the excitation of spectra in the extreme ultraviolet. More recently, this source has been used by Edlén[11] for the excitation of the most highly ionized atom for which the spectrum has yet been classified—eighteen times ionized copper, CuXIX.
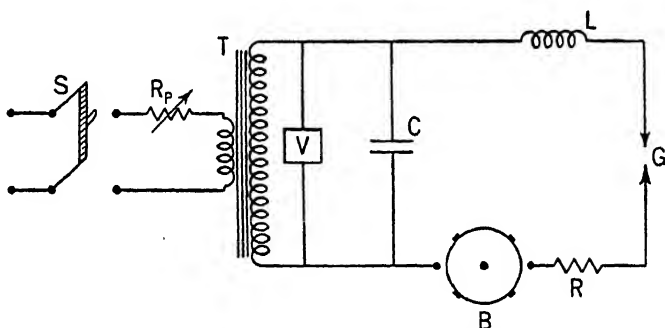
Fig. 4. **Controlled Spark Circuit.** S, primary switch; R_p, primary resistance; T, high-voltage transformer; V, electrostatic voltmeter; C, capacitance; L, inductance; B, synchronous rotating spark gap; R, damping resistance; G, spark gap for sample.

With the spark, as with the arc, any conducting solid electrodes may be used directly. Substances which are rare, nonconducting, powdered, or otherwise unsuitable for use as solid electrodes may be packed in a hollow carbon or aluminum electrode, alloyed with other material, or pressed or sintered with metal powders into a solid electrode.

The usual condensed spark, while generally steadier than the arc, does not always give the uniform and reproducible relative line intensities desired in quantitative spectrochemical analysis. To a large extent the variability seems to be attributable to lack of constancy in the number and in the rate of decay of the alternating arc discharges in the train following the spark breakdown at every half-cycle. Various devices have been used to stabilize the spark. One of the most successful, first introduced in spectroscopic work by Feussner,[12] is the synchronous auxiliary spark gap. In its simple form, the circuit, shown in Fig. 4,

[9] A. Fowler, *Phil. Trans.*, **225A**, 1, 1925.
[10] R. A. Millikan and R. A. Sawyer, *Phys. Rev.*, **12**, 167, 1918.
[11] B. Edlén, *Zeits. f. Physik*, **100**, 621, 1936.
[12] O. Feussner, *Arch. f. Eisenhüttenwesen*, **6**, 551, 1932.

differs only from the usual spark circuit by the addition of the rotating gap B, which is driven by a synchronous motor. The gap is closed only for a brief interval at the peak voltage of each half-cycle. The oscillating discharge train is damped out by an air blast or by other means. The resulting discharge is very steady and uniform in its characteristics and has been frequently used in precise spectrochemistry.[13]

14. Gaseous Discharges

Another large class of spectroscopic sources consists of the gaseous discharges, for all of which the prototype is the original Geissler tube. The arc in air is, in fact, an example of gaseous discharge, but the name is more commonly applied to discharges in gases at a reduced pressure. In a gas discharge, a sheath of ions near and surrounding the cathode marks the edge of the cathode fall within which electrons released from the cathode by ion bombardment attain sufficient speed to produce new ions by collisions with atoms. At the edge of the cathode fall appears a negative glow characterized by the appearance of many lines of these newly ionized atoms.

Outside this glow is the Faraday dark space, and beyond it, extending to the near vicinity of the positive electrode, is the positive column. If the discharge is extended in length, the positive column will extend to fill any length of tube—even many feet—while if the discharge is compressed, the positive column will be the first part of the discharge to contract and disappear. The positive column is the most conspicuous feature of most discharges and is responsible for most of the light emission. Compared with the cathode fall, it is a region of relatively low potential gradient and electron speeds, and hence one in which lines of the atom, or "arc" lines, predominate.

The positive column of a gaseous discharge is often used for observation of "arc" spectra of gases. To obtain more light, the column is often viewed "end-on" by placing the electrodes in side tubes or by using ring electrodes. The discharge may also be observed in a capillary or constricted region of the tube where the current density and hence intrinsic brilliance are increased.

In ordinary gaseous discharges, the pressure is usually a few millimeters or a centimeter of mercury. At much lower pressures—a few hundredths of a millimeter—a higher excitation may be produced by the periodic discharge of a condenser through the tube.

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[13] M. F. Hasler and H. W. Dietert, *J. Opt. Soc. Am.*, **33**, 218, 1943, describe an interesting modification of the interrupted-spark source in which a low-power, high-voltage interrupted spark is used to ignite and control a high-power, low-voltage spark which is connected in parallel and which has a capacity and resistance that are variable over wide ranges.

Again, if the cathode is made hollow (Fig. 5), it will be found that, as the discharge pressure is reduced, the discharge retreats within the cathode until, at a pressure such that the mean free path of the electrons is approximately the cathode diameter, the negative glow fills the hollow cathode. This hollow cathode glow, first used by Paschen, is characterized by low potential gradients and an almost pure electron excitation. The electron velocities are fixed by the critical potentials of the sustaining gas.[14] The material of the cathode, or of any metal lining it, is vaporized by bombardment of the gas ions and excited by electron collisions. When the rare gases are used and the gas pressure is properly regulated, the excitation is well adapted for the full development of high-series members of the spectra of singly ionized atoms. It has been so used
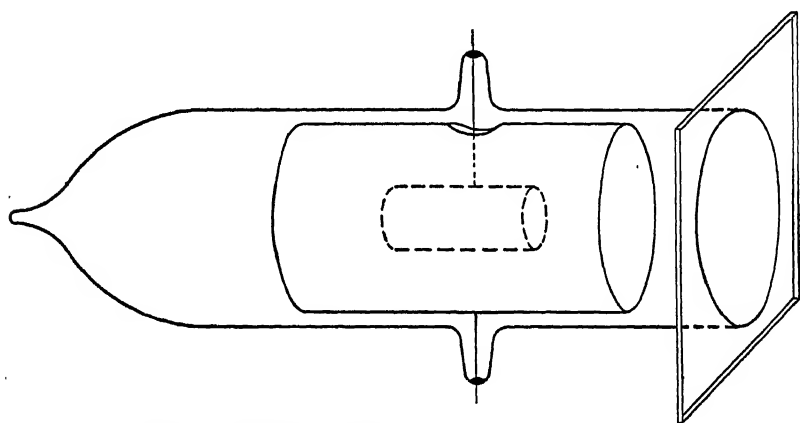
Fig. 5.   Paschen's Hollow-Cathode Discharge Tube.

by numerous observers. Since this source operates at a relatively low pressure, the tube can be placed directly before the slit of a vacuum spectrograph and used to excite series spectra in the extreme ultraviolet.[15]

The gaseous discharge may also be maintained in a closed vessel without electrodes (electrodeless discharge). The vessel may be of any convenient shape; it is wrapped with or placed inside a coil carrying a high-frequency current. The current may be generated by a vacuum tube oscillator or a Tesla spark generator. The coil current sets up in the tube an oscillating high-frequency electric field, which produces enough electron velocity to excite the gas atoms or molecules. The electron velocities depend on the field strength, the length of time the field is applied, and the distance an electron can travel before colliding with a molecule. These factors can be controlled by adjusting strength and frequency of the current and the gas pressure; accordingly, the type of

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[14] R. A. Sawyer, *Phys. Rev.*, **36**, 44, 1930.
[15] R. A. Sawyer and F. Paschen, *Ann. d. Phys.*, **84**, 1, 1927.

spectrum to be produced varies within considerable limits.   Any gas, or any metal which can be vaporized by the temperatures to which the tube can be subjected, can be used in the electrodeless discharge.   This discharge is convenient for rare gases, or for gases or vapors which attack electrodes or which may be contaminated by them.

15. The Choice of a Light Source

The choice of a light source for any particular use is determined by many factors, such as the nature and availability of the material to be excited, the physical limitations of size, enclosure, and surrounding gas, and the degree of excitation desired.   Many modifications of the fundamental sources have been used for particular applications and have been described in the literature of these applications.   The choice of a proper source is an important factor in any spectroscopic investigation and one which demands critical examination of the possibilities and limitations of those available.

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CHAPTER 3
Spectroscopic Apparatus—General Principles

16. General Theory: Definitions

Newton demonstrated, as was discussed in Chapter 1, that white light is a composite of light of all colors of the visible spectrum. In general, any light, unless it is monochromatic, is a mixture of various colors—or, better, radiations, since they are not necessarily visible radiations. These radiations differ from one another in wave length.

A *spectroscope* is an instrument which separates these different wave lengths, or disperses them into a spectrum for visual observation. A *spectrograph* is an instrument for producing a spectrogram, or photographic image of a spectrum. The chief structural difference is, that the spectroscope has an eyepiece at the focal plane where the image of the spectrum is formed, while the spectrograph replaces the eyepiece with a photographic plate at the focal plane.

The spectrograph, in general, consists of: (1) a dispersing device which gives to different wave lengths passing through it different emergent angles; (2) an optical system of mirrors or lenses to bring the different wave lengths to a focus; (3) an entrance aperture, usually a rectangular slit, whose images, formed by the optical system in light of different wave lengths, are the spectral "lines" which are observed or photographed.

In Newton's instrument the dispersing device was a glass prism; now prisms of a variety of transparent dispersing media are used. Fraunhofer introduced the grating as a dispersing device, and, as will be seen later, it is now used in various forms—transmitting and reflecting, plane and concave. Moreover, numerous interference arrangements other than gratings are employed to disperse light. Before passing to particular forms of spectrographs, however, it seems advantageous to discuss some properties of spectrographs, whatever their dispersing or optical systems, which are common to all of them because they are optical instruments.

An important characteristic of any spectrograph is its *dispersion*, or power to spread different wave lengths out so that they emerge from the dispersing system at different angles and are focused in different positions in the focal plane of the spectrograph. The difference in angles for different wave lengths is measured by the *angular dispersion* of the instrument, defined as $\Delta\theta/\Delta\lambda$, where $\Delta\theta$ is the difference in emergent

angles corresponding to a difference in wave length $\Delta\lambda$; or, in the limit, as $\Delta\lambda$ approaches zero, the angular dispersion may be expressed by the derivative form $d\theta/d\lambda$. The angular dispersion may be expressed in radians or degrees per angstrom unit, or in other convenient units of like dimensionality. The *linear dispersion* or separation of different wave lengths in the focal plane is expressed as $\Delta x/\Delta\lambda$, where Δx is the distance between two spectral lines which differ in wave length by $\Delta\lambda$. In the limit, as $\Delta\lambda$ approaches zero, this takes the derivative form $dx/d\lambda$. The linear dispersion is expressed in centimeters per angstrom or in other similar units. In general, if $d\theta/d\lambda$ is the angular dispersion produced by the dispersing system, and f the focal length of the optical system by
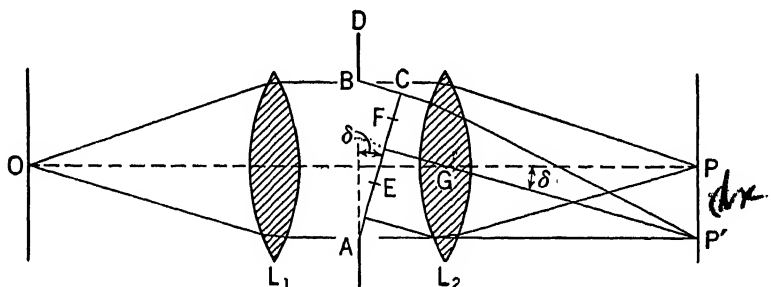
Fig. 6. The Diffraction of a Plane Wave by a Rectangular Aperture.

means of which the light is brought to a focus, the linear dispersion will be given by

$$\frac{dx}{d\lambda} = f\frac{d\theta}{d\lambda} \tag{1}$$

since dx is the chord of an angle of radius f and angular opening $d\theta$ and is approximately equal to the arc. Again, if $\Delta\theta$ is not too big, and f does not vary rapidly with wave length, we have

$$\frac{\Delta x}{\Delta\lambda} = f\frac{\Delta\theta}{\Delta\lambda} \text{ and } \Delta x = f\Delta\theta \tag{2}$$

(See Fig. 6, where $GP = f$, $PP' = dx$ or Δx, and $\delta = d\theta$ or $\Delta\theta$.)

17. Resolving Power

It would appear from these equations that, by making the focal length sufficiently large, it would be possible to separate two adjacent slit images, or spectral lines, due to light of two neighboring wave lengths, however little the wave lengths differed. Such, indeed, would be the case if a point were imaged by an optical system as a point, or, in the case of the spectrograph, if an infinitely narrow slit were imaged in the focal plane as an infinitely narrow line. In reality, however, an image is a diffraction pattern of a finite size which depends both on the wave length

of the light forming the image and on the dimensions of the optical system. A spectrograph of long focal length, then, may produce slit images of two adjacent lines which, in the ratio that they are farther apart, are also broader than the images formed by a similar instrument of shorter focal length. There is thus a limit to the power of an instrument to separate adjacent images of slightly different wave length. This power, known as the *resolving power*, is expressed as the ratio of the wave length observed to the smallest difference between two wave lengths which can just be resolved or distinguished as two separate lines. The ratio $\lambda/\Delta\lambda$ is, then, a pure number without dimensions, and may vary widely for different instruments, from a few hundred for a small prism instrument to a million or more for the most powerful interference spectrographs.

In any spectrograph, the actual resolving power may be computed directly from observations made with the instrument; or the theoretical resolving power may be calculated on the basis of suitable assumptions. As an introduction to such computations, the following case is of interest. Referring to Fig. 6, which represents the apparatus schematically in section, light from an infinitely narrow, self-luminous, vertical slit at O is rendered parallel by the collimator lens L_1. A plane wave front then passes through a rectangular opening in the screen at D, and the image is studied at the focal plane PP' of a second or camera lens L_2. The lenses are considered to be free from aberrations or image imperfections of any kind. The opening AB at D is the limiting stop in the system; that is, it is the only diaphragm which limits the size of the bundle of rays passing through the instrument. In the language of geometrical optics, this means that, seen from O, the image of AB formed by the lens L_1 must appear smaller than any other diaphragm image seen from O; and that from the focal plane PP', the image of AB formed by L_2 must appear smaller than any other image seen from that plane. If AB is the limiting aperture, the diffraction pattern will depend on the dimensions of AB only. In an actual spectrograph, the dispersing system is placed at D between the lenses, but may be neglected in this discussion since, if monochromatic light is considered, the behavior to be discussed is unchanged.

The light from all points of the opening AB reaches the point P on the axis in the same phase, since this is the focus of the geometrical wave front, and here the light intensity is at a maximum. However, in addition to the light at the geometric image P, there may also be light at points such as P', since, by Huyghen's principle, a diffracted wave front may be considered to spread in all directions from the aperture AB in the screen D. Thus a bundle of rays of section AC will be brought to a focus at P', since AC is perpendicular to the chief ray GP' through the center of the lens. All the light in this bundle, however, will not reach P' in the same phase, since rays passing through the upper parts of the opening

traverse a greater length of path than those passing through the lower parts.   If the distance BC is exactly one wave length of the light used, then for every point in the lower half of AC, such as E, there will be a corresponding point in the upper half F such that the light from F will have traveled just half a wave length farther than that from E, and the two rays will be thus exactly out of phase and will destroy or cancel each other.   Accordingly, the light passing the lower half of AB destroys that passing the upper half, and the result is a minimum of light at P'.

At a point below P' such that BC is $3\lambda/2$, the light intensity will again increase to a maximum, since now the bundle AC may be thought of as divided into three equal parts, two of which will destroy one another, as described above, while the third will provide light for a much weaker maximum than the central maximum.
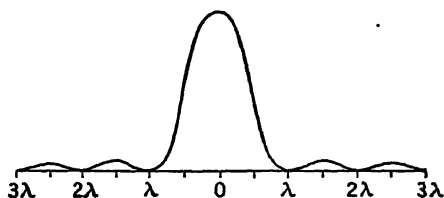

Fig. 7.   Intensity Distribution in the Diffraction Pattern of a Rectangular Aperture.

Again, when $BC = 2\lambda$, the light intensity will once more be at a minimum, since the bundle AC may be considered divided into four equal parts, two of which destroy the other two.

In general, then, the light intensity is at a maximum when $BC = (n + \frac{1}{2})\lambda$, and at a minimum when $BC = n\lambda$, where n takes the integral values 1, 2, 3, etc.

The image in the image plane, PP', of the vertical slit is therefore not a geometrical image of the slit, but a system of vertical fringes, whose intensity is represented diagrammatically in Fig. 7.   Since, in Fig. 6, the triangles ABC and GPP' are similar, if we let $AB = d$ the width of the aperture, and $GP = f$, the focal length of the lens, L_2, it follows that the successive minima are at distances from P such that $\sin \delta = n\lambda/d$, or approximately, for small values of δ,

$$x = n\frac{f\lambda}{d}, \, n = 1, 2, 3, \cdots \tag{3}$$

The successive maxima are at distances from P, approximately,

$$x = \left(n + \frac{1}{2}\right)\frac{f\lambda}{d}, \, n = 1, 2, 3, \cdots \tag{4}$$

The width of the first maximum is, then, $2f\lambda/d$ and is directly proportional to f and inversely proportional to d.

A detailed treatment of diffraction, with consideration of the form and relative intensity of the maxima and of apertures of different shapes, may be found in texts on physical optics.[1]

It is clear, then, that the spectral line image formed by any spectrograph is in reality a diffraction pattern. Equations (3) and (4) show that in the case discussed of an infinitely narrow, self-luminous slit, the line-image pattern depends on the optical system and the wave length. Actually, the slit cannot be either infinitely narrow or self-luminous, and, as we shall see later, the image pattern will depend both on the slit width and on the manner in which it is illuminated. In any case, however, usually only the central maximum of the pattern need be considered, since the lateral or outer maxima are much weaker. In the case discussed, the ratio of the intensity of the first lateral maximum on either side to the central one is

$$\left(\frac{2}{3\pi}\right)^2 = \frac{1}{22.2} = 4\%$$

and the intensity of the outer ones falls off in geometrical ratio.

If the images of two adjacent spectral lines in the focal plane of a spectrograph are so close that their central maxima overlap, the resultant illumination will 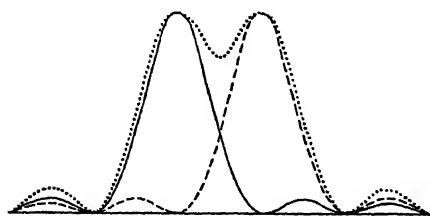be obtained by summing up the intensities of the two individual maxima. This pattern will be recognized as two lines if the two maxima appear as separate peaks, with a distinct dip or minimum between. It was proposed by the third Lord Rayleigh, as a criterion for use in the calculation of resolving power, that two lines might be considered to be resolved if the central maximum of one line fell on the first minimum of the other. This case is represented in Fig. 8 for two lines of equal intensity. The resultant intensity obtained by summing the two curves is shown by the dotted line. It is apparent that the dip between the two maxima, which here has 81 per cent of the intensity of either maximum, will disappear entirely if the two lines are much closer together.

Fig. 8. Resultant Illumination of Two Overlapping Diffraction Patterns, Shown by Dotted Curve.

Resolution by a spectrograph of two lines of slightly different wave length, λ and $\lambda + \Delta\lambda$, means, according to Rayleigh's criterion, that if the first maximum of wave length λ is formed by the spectrograph at an

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[1] Cf., for example, C. F. Meyer, *The Diffraction of Light, X-Rays, and Material Particles*, Chicago: The University of Chicago Press, 1934.

emergent angle θ, the first maximum of wave length $\lambda + \Delta\lambda$ is formed at an emergent angle $\theta + \Delta\theta$, where also is formed the first minimum of wave length λ. Referring to Fig. 6, the condition is that $\Delta\theta = \angle PGP'$ $= \angle BAC$, and since, for such small angles, the tangent may be written for the angle,

$$\Delta\theta = \frac{PP'}{GP} = \frac{BC}{BA} \text{ or } \Delta\theta = \frac{\lambda}{BA} \tag{5}$$

the computation of the theoretical resolving power of any actual spectrograph involves finding an expression for $\Delta\theta$ in terms of the constants of the dispersing system of the instrument. Rewriting the expression of page 30 for resolving power, $\lambda/\Delta\lambda$, in terms of angular dispersion gives

$$\frac{\lambda}{\Delta\lambda} = \frac{\lambda}{\Delta\theta} \cdot \frac{\Delta\theta}{\Delta\lambda} \doteq \frac{\lambda}{\Delta\theta} \cdot \frac{d\theta}{d\lambda} \tag{6}$$

Expression (6) is readily evaluated in terms of the dispersion of particular instruments, and examples will be given when such instruments are discussed.

This theoretical resolving power is often attained in the best instruments. Actual resolution, however, is affected by numerous factors, such as the relative intensities of the two adjacent spectral lines, their form or structure, the width of the slit, the mode of illumination of the slit, the perfection of the optics and their adjustment, the graininess or contrast of the photographic plate, and the power of the eyepiece used for inspection. Some of these factors will be discussed in other places. It may be noted here that, according to Equation (3), the width of the central diffraction maximum is proportional to f, the focal length of the camera lens, as is also the dispersion, by Equation (2). A lens of longer focal length may improve the resolving power of a spectrograph only if the diffraction patterns of the original lens are too fine for the resolving ability of the photographic plate or eyepiece used. If, however, the plate or eyepiece will resolve two patterns separated by Rayleigh's criterion (Fig. 8), any further increase of the focal length of the lens will increase the width of the line image in the same ratio as it increases the dispersion, and so will not improve the resolving power unless the aperture b of the system is also increased.

18. Brightness of Image

The intensity of illumination of the spectra produced by a spectrograph depends, of course, upon such characteristics of the instrument as the focal length and the aperture of the lenses, and the reflection and transmission losses within the instrument. The illumination depends also upon the way in which the slit is illuminated by the external light

source used. The effect of the method of illumination depends upon the general laws governing the brightness of images in optical instruments.

A spectroscopic light source radiates energy of one or more wave lengths at a rate which is expressed in terms of its *radiant flux F*. In visible photometry, the unit of flux is the *lumen*, which is the flux radiated into a unit solid angle by a source of one candle power. In spectroscopy, however, since the light may not be white, or even visible, a more general unit of luminous energy, such as the erg per second or the microwatt, is necessary.

The number of ergs per second which are equivalent to a lumen depends on the wave length or color of the light, being least in the green, where the eye is most sensitive. In regions of wave lengths to which the eye is not sensitive, no comparison of these units is possible.

The *luminous intensity* of a source depends on the amount of "light," or flux, which it gives off in a particular direction, and is measured for visible light in candles. If luminous intensity is I and solid angle in radians is ω, from the definition of the lumen,

$$I = \frac{F}{\omega} \tag{7}$$

or, if the solid angle is reduced in size, in the limit for the intensity along a ray,

$$I = \frac{dF}{d\omega} \tag{8}$$

For radiant energy in general, intensity may be measured in microwatts per solid angle rather than in candles.

This radiant energy falling on a surface produces an *illumination E* measured in terms of radiant energy per second per unit of area, or

$$E = \frac{dF}{ds} \tag{9}^2$$

Illumination may be measured for visible light in lumens per square foot (which are also called *foot-candles*) or, more generally, in microwatts per square centimeter.

Since all sources do not radiate equally in all directions, and since all illuminated surfaces do not reflect or transmit equally in all directions, the *brightness B* of a surface depends on the rate at which energy is sent out from the unit area (projected in the line of sight) in a particular direction, or

$$B = \frac{dI}{ds} = \frac{dF}{d\omega \cdot ds} = \frac{dE}{d\omega} \tag{10}$$

---

[2] If the flux is not incident normally, the right-hand side of this expression must be multiplied by cos θ, where θ is the angle between the surface normal and the flux. Then, $E = (dF/ds) \cos \theta$.

Brightness is thus either luminous intensity per unit projected area, or illumination per unit solid angle. The unit of brightness may be the *lambert*, which is the brightness of a surface emitting or reflecting one lumen per square centimeter; it may be the candle power per square centimeter, which is equivalent to π lamberts; or, in absolute units, it may be the microwatt per unit solid angle per square centimeter. A perfectly diffusing surface—that is, one which scatters uniformly in all directions the radiation falling on it—will appear equally bright and have equal brightness regardless of the angle at which it is viewed or of the size of the solid angle in which the radiation falls on it. A piece of mat paper approaches this condition. On the other hand, a perfectly reflecting surface will appear bright only if viewed in a direction along which some of the incident radiation is reflected, and will have zero brightness in other directions.

In the case of transmission of radiation through transparent surfaces or through apertures, the brightness of the beam, as viewed from behind the surface, depends, by Equation (10), not only on the rate at which energy is transmitted through unit area but also on the solid angle in which the energy is radiated. Accordingly, two identical sources, side by side, do not appear twice as bright as one—although they send twice as much energy to a given area—but only twice as large and of the same brightness. E, in Equation (10), is doubled, but so also is ω. Again, two images receiving energy at equal rates over equal areas may not be equally bright if the radiation converges in different solid angles; and, conversely, equal brightness of two images does not necessarily mean equal image energy per unit area.

19. The Illumination of the Spectrograph Slit

In most applications of the spectrograph, the fundamental quantity in determining the illumination of the spectra is the flux of energy per unit solid angle through the instrument. Of the light which enters the spectrograph through the slit, only that part can be effective which falls on the collimator lens. Any light beams which are outside the cone whose base is the collimator lens will not contribute to the spectral image and may appear as stray or scattered light. Higher brightness on the slit face does not necessarily mean brighter spectra unless it is accompanied by greater flux per unit solid angle.

The question commonly arises of how to attain the maximum illumination of the spectrum with a given light source and spectrograph. In general, there is no unique solution of the problem. It is, however, not difficult to assure that an optimum condition has been attained.

. The case may be considered first of a light source of considerable size and of uniform surface brightness which is used without a condensing lens. (The effect of any diffraction of the light by the slit is neglected here, but

will be treated later when slits and the question of slit width are discussed.) If the light source used is of large enough extent and can be brought so close to the slit that it subtends, at all parts of the slit an angle at least as large as the collimator lens does, the maximum possible illumination of the image will be attained, provided that the spectrograph is stigmatic (provided that it images a point on the slit as a point in the focal plane of the camera).

This condition for maximum illumination is illustrated in Fig. 9, which shows a spectrograph collimator (a) in section and (b) in elevation. If the slit is narrow in comparison with the lens diameter, its width
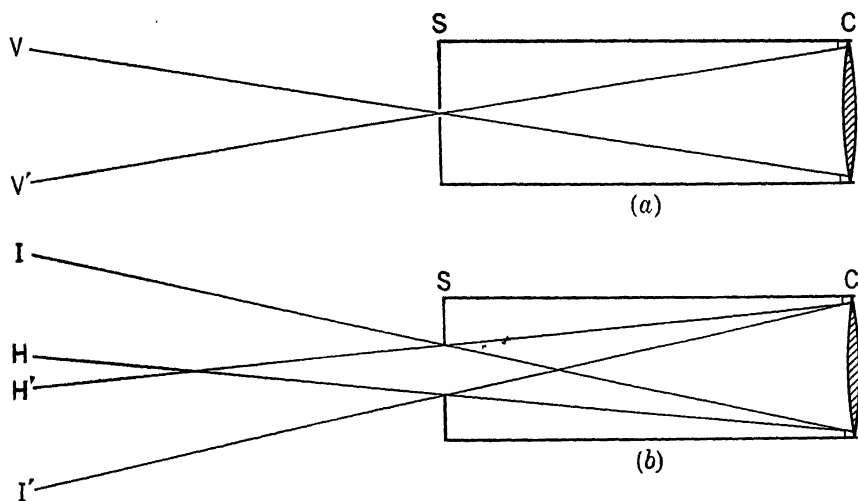

Fig. 9. Illumination of a Collimator through a Rectangular Slit: in Section (a), and in Elevation (b).

may be neglected. All the light entering the slit from any point which is in the region between the vertical planes V and V', defined by the slit edges and the sides of the collimator lens opening, and which is suitably located in the vertical plane, as described below, will enter the collimator aperture, while light from a point outside this region cannot reach the lens at all. In the vertical section, Fig. 9(b), is a region of full illumination, bounded by the planes VV' and the planes HH', which are fixed by the bottom of the slit and the bottom of the collimator lens and by their tops, respectively; from any point in this region all light entering the slit reaches the lens. Outside this region is a vignetted region, bounded by the planes VV' and by the space between the planes HH' and the planes II', which are fixed by the top of the slit and the bottom of the collimator lens, and by the bottom of the slit and the top of the collimator lens, respectively. Light from a point in this region

cannot reach all parts of the lens, and from outside II' no light can reach the lens.

A light source of uniform brightness, in any plane in front of the slit, of such extent that it covers the whole cross section of the region bounded by the planes VV' and II', sends the maximum amount of useful radiant energy into the spectrograph. The proof of this proposition is given in treatises on the subject[3] and will not be given here. It is apparent, however, that in the special case where the source radiates uniformly in all the directions from which rays reach the slit, and where the vignetted region is negligible, the effective area of the source increases with the square of the distance from slit to source, while the intensity of illumination reaching the slit from a unit area of source decreases with inverse square of this distance. The illumination entering the slit remains constant because the two effects cancel.

20. The Use of a Condensing Lens

When the light source is of sufficient size, as described above, to send the maximum amount of useful energy into the spectrograph, then no
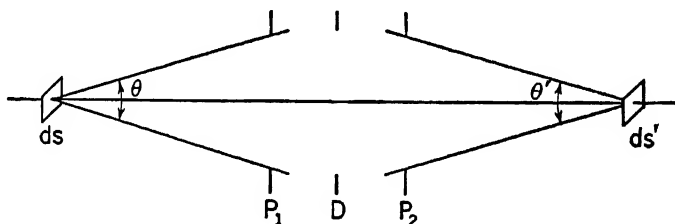

Fig. 10.   Image Formation in an Optical System.

condensing lens arrangement can increase this illumination. If, however, the source or the part of it which is to be used is too small to fill the collimator with light, then the use of a condensing lens to form an image of the source at or near the slit will increase the illumination of the spectrum. The maximum illumination from a given source is attained, with any condensing lens arrangement, when the collimator is filled with light. These statements can be proved by a calculation of the brightness of the image formed by a condensing system. Thus, suppose, in Fig. 10, that a source of area ds and brightness B forms through some optical system an image ds' whose brightness is to be found. The optical system is assumed to be free from aberration. Its aperture stop D is imaged at P_1 by that part of the system between D and ds, and is imaged at P_2 by that part of the system between D and ds'. As was explained

[3] M. v. Rohr, *The Formation of Images in Optical Instruments*, p. 541, London: H. M. Stationery Office, 1920, for a general treatment; J. R. Nielsen, *J. Opt. Soc. Am.*, **20**, 701, 1930.

on page 30, these images, known, respectively, as the entrance and exit pupils, limit the entering and emerging bundles of rays. If the optical system is a single thin lens D, P_1 and P_2 fall together at the lens rim itself. P_1 subtends an angle θ at ds, and P_2 an angle θ' at ds'. If P_1 be divided into elements of area da, comprised between concentric rings of radii ρ and $\rho + d\rho$ (Fig. 11), then

$$dF = Id\omega = Bdsd\omega$$
$$d\omega = \frac{da \cos \alpha}{r^2}$$

and

$$da = 2\pi r \sin \alpha \cdot rd\alpha$$

whence

$$dF = 2\pi Bds \sin \alpha \cos \alpha d\alpha$$

and

$$F = 2\pi Bds \int_0^\theta \sin \alpha \cos \alpha d\alpha$$
$$= \pi Bds \sin^2 \theta \qquad (11)$$

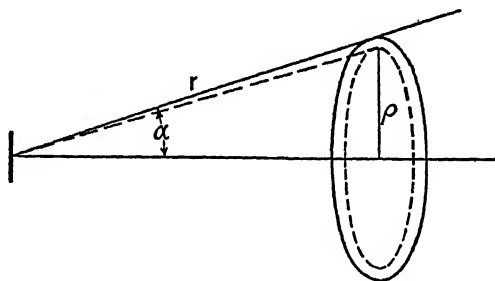Fig. 11.   Illumination of a Lens.

Likewise, since the image ds' is formed by radiation which emerges from the exit pupil P_2, subtending an angle θ' at ds'', the luminous flux through ds' is, then

$$F' = \pi ds' \sin^2 \theta' \qquad (12)$$

Neglecting any loss of light by reflection or absorption, $F = F'$, since all radiation entering P_1 passes P_2 and enters ds'; whence,

$$Bds \sin^2 \theta = B'ds' \sin^2 \theta'$$

Now it is shown in texts on geometrical optics that, if the optical system forms an aberrationless image of ds at ds', $ny \sin \theta = n'y' \sin \theta'$, where n and n' are the indices of refraction on the two sides of the system, and y and y' are the size of the object and of the image, respectively.

Also, since

$$\left(\frac{y}{y'}\right)^2 = \frac{ds}{ds'}$$

it follows that

$$\frac{B'}{B} = \left(\frac{n'}{n}\right)^2 \tag{13}$$

If, as is usually the case, both ds and ds' are in air, $n = n' = 1$, and $B = B'$. Thus, regardless of the optical arrangements, it is impossible to produce an image of greater brightness than the source, and, in fact, because of losses in the system, the brightness will actually be less. This important theorem, in a simpler form which shows that no optical instrument can increase the natural brightness of an object as seen by the unaided eye, is very old and has been attributed to Robert Smith, who stated it in his *Optics*.[4]

The theorem is so important that a simpler, less mathematical, and less exact proof will be given for the case of a simple condensing lens, used to focus on a slit an image of a luminous source.
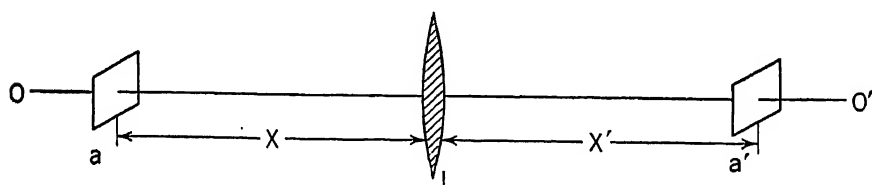

Fig. 12.   Image Formation by a Single Lens.

The source of area a, at a distance x, is imaged as an area a' at a distance x' by the lens L of area A (Fig. 12). It is assumed that a and a', as well as L, are normal to the optical axis OO', and that equal areas of L receive from a and radiate to a' equal amounts of energy, regardless of the inclination of the beams. The energy flux falling on the lens is then

$$F = I\omega = Ba\omega = Ba\frac{A}{x^2} \tag{14}$$

and the energy flux from the lens to the image a' is

$$F' = I'\omega' = B'a'\omega' = B'a'\frac{A}{(X')^2} \tag{15}$$

Since, neglecting losses, all energy striking L is concentrated in a', these fluxes are equal,

$$Ba\frac{A}{x^2} = B'a'\frac{A}{(x')^2} \tag{16}$$

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[4] Robert Smith, *A Compleat System of Optics*, Cambridge, 1738. Book II, Ch. V, pp. 255–261.

or

$$\frac{B'}{B} = \frac{a}{a'}\left(\frac{x'}{x}\right)^2 \tag{17}$$

But since the linear size of the image y is to the linear size of the object y' as their distances from the lens,

$$\frac{y}{y'} = \frac{x}{x'} \text{ or } \frac{a}{a'} = \left(\frac{x}{x'}\right)^2 \tag{18}$$

and therefore,

$$\frac{B'}{B} = 1 \tag{19}$$

Thus, regardless of the focal length or diameter of the lens or of the relative distances of source and image from the lens, the brightness of the condensed image is, disregarding reflection and absorption losses, the same as that of the source.

21. The Conditions for Maximum Illumination and Maximum Intrinsic Energy of a Spectrum

The conditions for maximum illumination of a spectrum under various conditions may now be summarized.   Since brightness is radiant power per square centimeter per solid angle, the maximum useful power from an element of the slit will be sent into the spectrograph when the solid angle in which energy is sent through the slit by the source or by the condensing lens is as large as the solid angle which can be accepted by the collimator, that is, as the angle subtended at the slit by the collimator lens.

It is true, however, that for a given lens and a given source–image distance, more luminous energy may be concentrated in the condensed image on the slit by using shorter image distances (the distance between the lens and the image) and so producing smaller images.   In such a case, the energy flux or power falling on the condensing lens is, by Equation (15),

$$F = Ba\frac{A}{x^2}$$

and thus flux is condensed on an area a', which may be expressed in terms of the source area, and of source and image distances, by Equation (18) as

$$a' = a\frac{(x')^2}{x}$$

The radiant power per unit area in the image is

$$\frac{F}{a'} = \frac{Ba\dfrac{A}{x^2}}{a\left(\dfrac{x'}{x}\right)^2} = \frac{BA}{(x')^2} \tag{20}$$

and is inversely proportional to the square of the image distance. The intrinsic energy of the image is thus increased by shortening x'; and, if the image is viewed on a diffusing screen, as on a white card, it appears more intensely illuminated, and if it is photographed, the photographic effect is greater, since the latter depends on total energy. But, from Equation (13) or Equation (19), this greater energy per unit area does not send more energy through the spectrograph, because the energy flow per unit solid angle is unchanged and, as soon as the collimator solid angle is filled, the additional energy does not fall on the collimator, since it passes through the slit at too great an inclination, and is merely wasted. The question of the best size of image to form on the slit may be fixed in particular cases by the characteristics of the spectrograph, the available equipment, or the desire to examine a particular part of the source.

It has been assumed above that the source will be imaged on the slit, as is, of course, essential if a definite part of the source is to be examined. Such imaging is not always exactly possible, especially if the condenser is not achromatic and so does not focus all colors in the same plane. The maximum flux of energy through the collimator lens may still be obtained under these conditions if the image of the source is formed at such a point that it subtends at the slit a larger angle than does the condensing lens.[5] The image may be either before or behind the slit; if it subtends a greater angle at the slit than does the condenser, the illumination may be considered to be the same as that produced by replacing the condenser lens by a luminous source of the same area and brightness. Obviously, the condensing lens, whatever its position or focal length, should, for maximum illumination, cover the entire section at its location enclosed by the planes VV', II' of Figure 9.[6]

22. Illumination by a Point Source

A surface source of finite area has been considered above. An interesting case occurs when the source is a distant luminous point, as in the case of a star. If this is imaged on the slit by a lens, the image will be a diffraction pattern, the dimensions of which depend, as pointed out on pages 30ff. for a slit, not on the size of the object but on the focal length and diameter of the condenser lens used. The central maximum from a circular lens of diameter d and area A is a circle of diameter $2.44 f\lambda/d$,[7] and it is surrounded by alternate dark and light circular bands or fringes. The energy flux from the star falling on the lens is, as in Equation (14),

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[5] P. H. van Cittert, *Zeit. f. Physik*, **69**, 298, 1931.

[6] See Abbe's First Law of Radiation, of which these above relations are a consequence, v. Rohr, p. 547.

[7] C. F. Meyer, *The Diffraction of Light, X-Rays, and Material Particles*, p. 90. Chicago: The University of Chicago Press, 1934.

$$F = I\omega = \frac{IA}{r^2} = \frac{\pi I d^2}{4r^2} \qquad \qquad (21)$$

where d is the diameter of the lens and r the distance to the star of candle power I.

The radiant power per unit area in the image, assuming it to be uniformly distributed over the central maximum, which is, of course, an approximation, is

$$\frac{f}{a'} = \frac{\pi I d^2}{4r^2} \div \left(\frac{2.44 f\lambda}{d}\right)^2 \frac{\pi}{4} = \frac{I d^4}{(2.44 f\lambda r)^2} \qquad (22)$$

This is seen to be proportional to d^4 and inversely proportional to f^2; hence, it is greatly increased by using a lens of larger aperture. Thus larger telescopes permit the photographing of fainter stars, since the stars' images are greatly enhanced relative to the intensity of their background, which follows the laws of extended sources.

Furthermore, the brightness of the star image will also be increased by a larger lens. Brightness, by Equation (10), is flux per unit area per unit solid angle. Using the expression of Equation (22) for F'/a', and noting that the solid angle in this case is $\pi d^2/4f$, we have

$$B' = \frac{F'}{a'\omega'} = \frac{I d^4}{(2.44 f\lambda r)^2} \div \frac{\pi d^2}{4f} = \frac{4 I d^2}{\pi f (2.44 \lambda r)^2} \qquad (23)$$

Everything on the right-hand side is constant except d^2, and thus B' is proportional to d^2, and therefore the energy flux per solid angle in the spectral image increases with the area of the condensing lens used so long as its angular aperture, or angle subtended at the slit, is equal to or less than that subtended by the collimator, so that all light from the condensing lens will be accepted by the collimator. If the telescope is of excellent quality and the atmospheric conditions good, the stellar diffraction image on the slit will be very small, and, in consequence, the spectral lines will be very short. Plaskett[8] has observed of the use of the stellar spectrograph with the 72-inch Victoria Observatory reflecting telescope: "The driving is perfect, without a trace of periodic or other error. The following is so close, the figure of the mirrors and the seeing generally so good, that it is necessary to set the driving clock slightly fast or slow, else the image remains so nearly in one position on the slit, which subtends an angle of $.3'' \times 3''$, as to produce too narrow or unevenly exposed spectra."

23. Illumination by Sources of Finite Depth

So far, only sources of negligible depth along the optical axis have been considered. Spectroscopic sources, however, are often of con-

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[8] J. S. Plaskett, *Astrophys. J.*, **19**, 209, 1919.

siderable depth, as in long discharge tubes viewed "end-on"; and, since only a small increment of this depth can be focused on the slit, the question arises as to the best choice and best arrangement of a condensing lens in this case. This problem has been discussed by Nielsen (*loc. cit.*), whose results are utilized here.

As was pointed out on page 36, any surface source will produce the maximum slit illumination, no matter what its distance from the slit, if it is large enough to cover the whole cross section bounded by the planes VV', II' of Figure 9. If the source extends in depth along the optical axis, and if each cross section satisfies the above condition, the amount of light is again a maximum, independently of the distance from the slit, and is proportional to the depth of the source along the optical axis, unless there is appreciable absorption or scattering of light within the source. As in the case of a surface source, a condensing lens is of use only when the source is not extended enough in cross section or cannot be brought close enough to the slit to satisfy the above conditions. Obviously, only one plane in the source at right angles to the optical axis can be imaged on the plane of the slit. However, as was pointed out on page 41, even if the source is not focused on the slit, it will be equally effective if its image subtends a larger angle at the slit than does the condensing lens, and it will produce maximum illumination if its image, real or virtual, covers the cross section bounded by the planes VV', II', when the image is in front of the slit or behind the collimator lens; the source will also be effective if it covers the cross section bounded by the planes VV', HH', when the image lies between the slit and the collimator lens. The last two statements are equivalent, of course, if the condensing lens covers at its location the cross-sectional area of the planes VV', II'. Various sections of a deep source are focused at different distances from the slit, and analysis by the above criteria shows how effective each section is.

Such questions as the best choice of a focal length and position of a condensing lens or the maximum effective length or best position of a long light source may readily be answered by the application of these conditions and the use of the simple lens formula. Often graphical treatment of the problem is convenient. Calculations for specific cases are found in Nielsen's paper. In general it may be said that with a suitably chosen condensing lens, correctly placed, it is possible to utilize the full amount of light from a longer source than is possible without a lens, and that the best arrangement is with the back surface of the source focused on the slit.

24. Types of Slit Illumination

In the preceding discussion, and particularly in the treatment of sources of negligible depth, it has been assumed that the source would

be imaged by the condensing lens on or near the slit.   Thus, a single point in the source illuminates one and only one point on the slit, and this one point on the slit then forms one and only one point in the spectral line image produced by the spectrograph (Fig. 13).   In Figure 13 the spectrograph optics are represented, for simplicity, only by the lens system, which is shown forming a spectral line image.   Any stigmatic dispersing or diffracting devices do not affect the principles of illumination here discussed, but would, in general, result in the formation of individual monochromatic images.   The path of the extreme rays from an axial point of the source to the formation of the axial point of the spectral line image is shown.   The one-to-one correspondence provided between points on the spectral line, the slit, and the source is essential if the spectra of particular points in the source are to be studied.   This arrangement also utilizes the maximum solid angle of radiation from a source
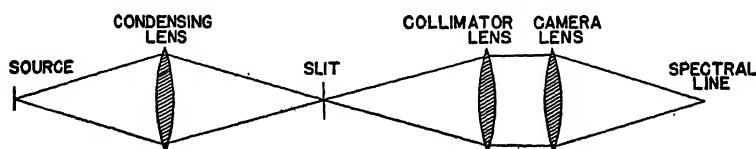

Fig. 13.   Spectrograph Illumination by Formation of Source Image of Slit.

point which the spectrograph can accept.   There are, however, conditions under which this mode of spectrograph illumination may be unsatisfactory.

In the first place, since each point on the slit is illuminated by a different point on the source, uniformity of illumination along the length of the slit, and hence of the spectral line, demands uniform luminous intensity over the area of the source used.   Such uniformity is not often found in light sources of the gas-discharge type.   Uniform illumination along the slit is, however, desirable in line photometric work where a rotating sector or step slit is used, and in some types of hyperfine structure and other research.   A second difficulty is that, since every part of the collimator lens and other optics contributes to each point of the image, a defective area in any component of the optics may result in marked inhomogeneities and irregularities in the spectral line image, and may even render a sharp image impossible.

In another mode of illumination which greatly reduces the first of these difficulties, a condensing lens is placed directly before the slit, and forms an image of the light source on the collimator lens (Fig. 14). It will be observed that each point of the source sends light to each point of the slit and each point of the spectral line.   Thus, except for the effect of variation of α and r (Fig. 11), the illumination should be uniform along the slit and along the spectral line.   It will also be seen that an area of the collimator lens as large as the image of the source on

that lens is effective in the illumination of each point of the spectral line. If this image is smaller than the whole area of the lens, the lens is in effect stopped down and the aberrations minimized. Similar stopping down can, of course, be accomplished in the first illumination scheme, Fig. 13, by a diaphragm placed at the collimator lens. Stopping down the lens in either case reduces the illumination, and the resolving power, from the maximum attainable.

In the first arrangement, the source need only be so extended that its image covers the width of the slit. The maximum illumination can be attained if the condensing lens has a large enough aperture to fill the collimator lens. In the second arrangement, maximum illumination requires that the image of the source cover the entire aperture of the
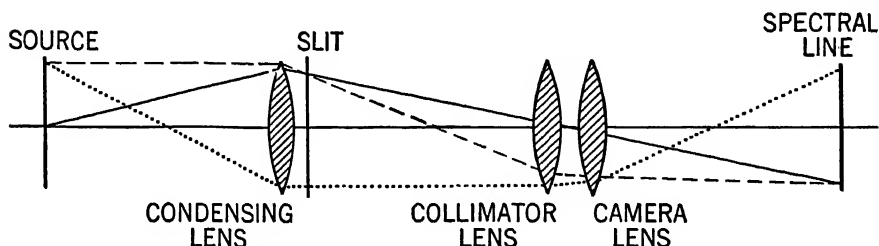

Fig. 14. **Spectrograph Illumination by Formation of Source Image on Collimator.**

collimator lens. If this image is of uniform brightness, a little consideration will show that the illumination will be the same as with a filled collimator lens in the first scheme, since the rate of flow of energy through the slit is the same in either case. Numerous modifications of one or the other of the two methods of illumination described have been devised to meet particular requirements.

25. Photographic Speed of Spectrographs

The brightness of the spectral line image produced by a spectrograph, as discussed above, cannot, barring reflection and transmission losses, be increased by altering the arrangement or size of the optics used. The photographic speed, however, depends on the total power per unit area $B\omega$, or illumination, and can obviously be increased by increasing ω, the angular aperture of the radiant bundle, as is done to obtain more rapid camera lenses. Spectrographs are often made symmetrical, that is, with the collimator lens L_1 (Fig. 6) and the observing or camera lens L_2 of the same diameter and focal length, a construction which results in a spectral line of the same size as the slit. High speed in a symmetrical spectrograph then obviously requires both collimator and camera lenses of large angular aperture; and, as the cost of lenses increases rapidly with the angular aperture, the cost of such high-speed, high-dispersion instruments may become prohibitive. Furthermore, the angular

aperture of the condensing lens must be larger than that of the collimator lens, since the condenser works at a distance greater than its focal length, while the collimator works at its focal distance. Thus, it is difficult to condense the light for a high-speed collimator.

To avoid the difficulties noted above, it is often advantageous when high photographic speed is needed, to make the spectrograph unsymmetrical. We may apply the argument of page 40 to the case of spectrograph speed, since, for light of any one color, the spectrograph may be thought of simply as a system which images the slit in the spectral line. Then from Equation (20), writing for x', the focal length of the camera lens, f_2, the radiant power per unit area in the spectral line image is BA/f_2^2, and thus depends only on the brightness of the slit illumination, the area of the camera lens, and its focal length. Since $A = (\pi/4)d^2$, this gives indeed the familiar camera rule that exposure is inversely proportional to $(f/d)^2$, or the "f/-number" squared. The photographic speed of a spectrograph is thus quite independent of the collimator focal length.[9] There are, then, with a camera lens of high angular aperture in a spectrograph, several advantages in using a collimator lens of longer focal length and consequently smaller angular aperture. The lens is cheaper, and it is easier to fill with light, since a condensing lens of small aperture is used.

The collimator lens of smaller angular aperture is also likely to have less spherical aberration and coma than a lens of large aperture, and hence is likely to lead to better spectral line images.[10] Further, since the dimensions of the spectral line are to those of the slit as the ratios of the focal lengths, a larger slit may be used with a collimator lens of long focal length to give the same size spectral line as that obtained by a finer slit with a collimator lens of short focal length. The larger slit requires less careful machine work and adjustment. Finally, the diffraction pattern of the wider slit is narrower than the diffraction pattern of the narrower slit, and this fact may have an important bearing on the illumination, as will be pointed out when slits are discussed.

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[9] See, for example, J. R. Nielsen, *J. Opt. Soc. Am.*, **20**, 701, 1930; J. W. Perry, *Trans. Opt. Soc.*, **33**, 159, 1932.

[10] A. C. S. van Heel, *Revue d'Optique*, **12**, 49, 1933.

CHAPTER 4
Prism Spectroscopes and Spectrographs:
Theory and Construction

The earliest spectroscopes and spectrographs were prism instruments, and this type is still important in point of numbers and in point of the variety and value of their applications. They will therefore be discussed first, although much that is said about the slit and the lenses is equally applicable to other forms of spectrographs.

Newton's apparatus consisted of a slit, a prism, and a single lens which was placed close to the prism (on either side) and which focused an image of the spectrum on a screen. Fraunhofer (1819) replaced the lens-and-screen arrangement by a telescope—actually part of a theodolite —with an eyepiece in which the cross hair could be illuminated. A great improvement was thereby effected, since the lines could be observed through the magnifying eyepiece, and since the theodolite mounting allowed precise measurements of angles and thus permitted quantitative descriptions of spectra and determinations of refractive indices. Both arrangements, however, suffered from the fact that, since the beam of light in the prism is not parallel, astigmatism is introduced by the prism. Babinet in 1839[1] appears to have been the first to overcome this defect by using, to view the spectrum, both a collimating lens with the slit at its focal point and a telescope. This arrangement is the modern form of the spectrograph, but its advantages were not immediately recognized and the older forms continued to be used. Kirchhoff and Bunsen's first apparatus, however, used both collimator and telescope, and following them the form was generally adopted with various refinements for adjustment and for measurement of angles. The spectroscope or spectrograph, then, consists of a slit, a collimator lens, a prism or prisms, and a camera (or telescope) lens, together with an eyepiece if the instrument is used for visual observation. The characteristics of these parts will be discussed separately.

26. The Slit

Fundamentally, the slit is a narrow, rectangular aperture which admits light to the spectrograph. The images of the slit formed by

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[1] J. Babinet, *Comp. Rend.*, **8**, 710, 1839.

the spectrograph after the light has been dispersed are the spectral lines. It is essential, then, that the edges of the slit be straight and parallel, in order to give a clean image, and that they be sharp, to avoid reflection of light from the edges into the spectrograph. Reflections from blunt edges tend to give broad and fuzzy lines; if the blunt edges are flat enough and properly inclined, they may, indeed, result in an apparent tripling of the spectral lines, the blunt slit edges acting as additional slits on either side of the real slit. It is also desirable that the slit be adjustable in width, and that, when the width is changed or when the slit is opened for cleaning, the jaws remain strictly parallel and return to an identical setting on readjustment. Careful design and good mechanical work are required to fulfill these requirements in the limited dimensions desirable.

The Bausch and Lomb Optical Company have used a slit which meets, in a very simple way, all the requirements listed above except that of adjustable width. Four standard fixed slits of two, five, ten, and twenty microns in width are cut in a properly protected silver coating deposited on a single quartz slide. The slide is mounted with the metal coating on the inner surface. The outer exposed surface is readily cleaned of any deposits; the inner surface can be cleaned if necessary. Stability and parallelism are insured. The quartz slide also serves to seal the instrument from dust. Four such fixed slit widths are satisfactory for most spectroscopic work, especially with instruments of low dispersion, and the use of such ruled slits does away with much of the difficulty of mechanical slits. Baird Associates, of Cambridge, Massachusetts, provide for use with their Eagle mounting of the concave grating a series of fixed slits of 25, 50, 100, and 200 microns width. The slits have stainless steel jaws and are mounted on metal plates which are readily interchangeable.

Adjustable slits will probably continue to be preferred for research work and for instruments of high dispersion, since, as we shall see, the proper slit width for best results will depend on the wave length used as well as on the kind of work at hand. The adjustable slit is formed by two jaws, mounted in parallel ways and so designed as to insure parallelism of motion. One, or both, of the jaws can be moved by means of a screw which controls the adjustment of the width. Unilateral slits, with one moving jaw, are simpler in construction than bilateral ones, with both jaws moving symmetrically. The bilateral type is to be preferred for some purposes, however, since the center of the spectral lines remains fixed when the slit width is varied.

Although quartz has been suggested as a material for slit jaws,[2] metal jaws are generally favored because of their greater strength. The metal should be noncorrosive and capable of taking a sharp edge and a high

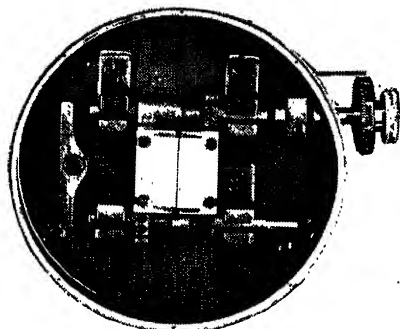[2] W. Crookes, *Chem. News,* **71,** 175, 1895.

polish. Monel metal, stainless steel, stellite, and nickel are often used.

It is extremely desirable that the slit be opened by the adjusting screw and closed by a spring of some type. This spring is interposed between the screw and the slit jaws and prevents the damage that would result to the jaws if they were closed directly by the screw. The screw should have a micrometer head—preferably reading in hundredths or thousandths of a millimeter, so that the slit width can be determined—and a stable, readjustable zero point.

Ways should be provided in front of the slit to carry diaphragms of various sorts for limiting the length of the slit or for exposing different parts of it to different radiations. Such diaphragms should be sharply focused in the same focal plane as the spectra in order that the spectral lines limited by them may be sharply terminated. The ways carrying the diaphragms should therefore be arranged to hold the diaphragms as close to the slit surface as possible.

Courtesy of the Bausch and Lomb Optical Co.

Fig. 15. **Bilateral Slit, with Protective Cover Removed.**

Such mounting is not always possible or convenient. The alternative is to use an additional lens, preferably an achromat which focuses a distant diaphragm on the slit. An example of such an illuminating system is shown on page 260.

If the condensing lens is to be placed directly before the slit (page 44), it is desirable to have a means of attaching this lens rigidly to the slit head. Such a mount avoids the danger of motion of the lens and also helps to keep dust from the slit. The lens mounting may be attached by screws (Bausch and Lomb) or may be in the form of a cap to slip over the lens head (Carl Zeiss). It should be readily removable and provide for the substitution of different lenses to compensate for different light-source distances. A slit of simple and sturdy design, supplied by the Bausch and Lomb Optical Company with their prism spectrographs, is shown, with its quartz cover plate removed, in Fig. 15. The slit is bilateral and has stellite jaws operated by a micrometer screw with a drum head graduated to indicate slit width in units of .01 mm. Slit widths can be estimated to single microns. The jaws are opened by the micrometer screw and are spring-closed, so that there is no possibility of damaging the jaws by closing the slit too tightly. The slit cover also carries just behind the cover glass a metal slide, which has a stepped opening for adjusting the slit length as well as a series of five staggered openings. Movement of the slide brings these openings in turn over

adjacent portions of the slit length. Five exactly contiguous spectra of five different sources can thus be recorded for visual comparison or measurements. Such an arrangement of slit openings, due to Hartmann and known as a Hartmann diaphragm, is extremely useful and commonly employed with stigmatic spectrographs.

27. The Collimator Lens

The function of the collimator lens is to render parallel the light from each point of the slit, so that the light bundles of every color incident on the prism shall all appear to come from a light source at an infinite distance. The prism system introduces no astigmatism in a parallel beam; accordingly, a point on the slit can be imaged as a point in the spectral line image rather than as a line—as is the case if astigmatism is present. Strictly, it is not possible, from an actual lens, to get a parallel beam for all colors and apertures, and whether the condition of parallelism is attained more or less accurately in any particular case depends on the structure of the lens and on the limitations of design and the choice of materials.

The problem of the collimator lens design is almost exactly that of a telescope lens, for the function of one is the exact reverse of the function of the other. The collimator lens has to render parallel the beam coming from a small plane object close to the lens axis, while the telescope lens has to form a small plane image of an object so distant that the rays from it may be thought of as parallel. A good telescope objective makes a good collimator lens, and the defects and technical difficulties of the one are largely those of the other, although, in either case, special conditions may influence the design.

It is outside the province of this work to discuss in detail the design of lenses. The chief image defects will, however, be discussed briefly in their relation to spectrograph design.[3] For collimator lenses, these defects are chiefly three: chromatic aberration, spherical aberration, and coma.

Chromatic aberration arises from the fact, discovered by Newton, that transparent media have different indices of refraction for rays of different wave lengths. Thus, since the focal length of a lens is a function of the index of refraction, a simple lens which renders rays of one color parallel cannot do so for rays of other colors, but will leave them somewhat divergent or convergent. Chromatic aberration may be overcome by using in a lens two materials with different dispersions or rates of change of index of refraction with wave length, $dn/d\lambda$. By using a

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[3] For a fuller treatment, see, for example, Hardy and Perrin *The Principles of Optics*, McGraw-Hill, New York, 1932, Ch. VI, or, for a general treatment, J. P. C. Southall, *Principles and Methods of Geometrical Optics*, Macmillan, New York, 1913.

positive lens of the less dispersive material and a negative lens of the more dispersive, a combination may be made which will have the same focal length for two colors. The focal length for all other colors will, however, differ somewhat from this focal length, and this difference gives rise to what is known as *secondary achromatism*. Nevertheless, the uncorrected variation in focal length will be much less than that of a simple lens. Such a combination lens, corrected for two colors, is called an *achromatic lens*.

Telescope lenses for visual work are usually corrected for the red Fraunhofer C line, 6563A, and the blue-green F line, 4861A, and show a residual small secondary aberration throughout the visible region. Photographic lenses are often corrected for the yellow D lines, 5893A, and the violet G line, 4341A, since this range gives the best compromise between the range of greatest visual sensitivity, which is in the yellow-green, and the range of greatest photographic activity, which extends far into the ultraviolet to a limit set in the case of glass lenses by the absorption of the glass. Outside the range of chromatic correction, the variation of focal length with color is much more rapid than within the range, although not so great as in an uncorrected lens.

It is possible, with a triplet lens of three properly chosen glasses, to bring three or more colors to a focus at the same point. Such lenses, called *apochromats*, are little used in spectrographic apparatus. Their added expense is seldom justified, since the function of a spectrograph is to disperse the various colors and bring them to a focus at different points along the photographic plate. A variation of focal length with wave length can often be allowed for by tilting or bending the plate, or both, to compensate for any lack of achromatism.

Chromatic aberration in glass lenses is conveniently corrected by combining a crown glass converging lens with a diverging one of flint glass. The choice of materials for use in the ultraviolet region, where glass is no longer transparent, is much more difficult. Quartz, which is transparent to about 2000A and is relatively abundant in large crystals, is the commonest selection. In combination with quartz, almost the only solid materials used are fluorite (calcium fluoride) or rock salt, both of which are transparent to even shorter wave lengths than is quartz. However, rock salt, for protection from the moisture in the atmosphere, must be enclosed between two quartz lenses in a tight cell, with the ever-present risk of failure of the seal at the edges. Fluorite, on the other hand, while very satisfactory, is hardly a commercial article in optical quality because of its scarcity, especially in crystals of over an inch in size.

As a substitute for natural fluorite in achromatic combinations with quartz, artificial lithium fluoride crystals have been used by C. H. Cartwright.[4] Lithium fluoride has been successfully prepared in large crystals

[4] C. H. Cartwright, *J. Opt. Soc. Am.*, **29**, 350, 1939.

by Kyropoulos[5] at the University of Göttingen, by Stockbarger[6] at the Massachusetts Institute of Technology, and by K. Chamberlain[7] at the University of Michigan. It is reported by Cartwright that a quartz-lithium fluoride-quartz achromatic triplet gives a very small secondary chromatic aberration over the great range 1800A to 16,000A, and that it also may be corrected for coma and spherical aberration. Lithium fluoride is transparent into the ultraviolet to about 1200A. It has been combined with calcium fluoride (fluorite) by Cartwright to make an achromatic doublet for the region 1300A to 1800A. As yet lithium fluoride, like fluorite, is hardly a commercial article, and achromatic lenses employing it have not been used in stock spectrographs.

The difficulties encountered in the use of transparent solids in combination with quartz have led to some use of liquids. The chief difficulty, aside from the added expense and difficulty of sealing the liquid between quartz plates or lenses, is that of temperature control. Some of the liquids have large temperature coefficients of refractive index,[8] and in all liquids temperature variations may cause convection, with resulting loss of definition. Quartz-water achromats have been used by Kipp and Zonen[9] of Delft, Holland, in an interesting spectrograph of large aperture, which will be described more fully later (page 88). In this design by van Heel, quartz-water combinations were used successfully both in the camera and in the collimator lenses.

As a result of the lack of suitable ultraviolet transmitting materials to combine with quartz, all large quartz spectrographs, and most small ones, are now made with simple quartz lenses, and a tilted plate is used to compensate for the chromatic variation of focal length with wave length.

A far more serious error in spectrograph lenses is that of spherical aberration, which is the failure of the lens to bring to a focus, at the same point, the rays which pass through zones at different distances from the axis. In the case of the simple biconvex lens with spherical surfaces, parallel rays which pass through zones farther and farther from the optical axis are brought to a focus progressively nearer to the lens (see Fig. 16). The result is that a distant point is not imaged as a point on the axis but as a range of points along the axis; on a screen placed at the best focus, the image is seen as a blur circle. On the other hand, a collimator lens, the function of which is to render parallel all the rays which reach it from a point on the slit, will, because of spherical aberration, fail to do so for some rays, to an extent which depends on the distance from the axis of the effective zone of the lens. Thus, if the rays

[5] S. Kyropoulos, *Zeits. f. Anorg. u. Allgem. Chem.*, **154**, 308, 1926.
[6] D. C. Stockbarger, *Rev. Sci. Inst.*, **1**, 133, 1936.
[7] K. Chamberlain, *Rev. Sci. Inst.*, **9**, 322, 1934.
[8] See page 65.
[9] A. C. S. van Heel, *Revue d'Optique Theor. Instr.*, **12**, 49, 1933.

passing at one distance from the axis emerge as a parallel bundle, those passing through inner or outer zones will be left either slightly convergent or slightly divergent. The result will be, of course, that after the rays have traversed the dispersing system, this lack of parallelism will persist in each colored bundle, and the camera lens, even if perfect, will fail to produce a sharp spectral line or slit image. A diverging lens produces spherical aberration opposite to that described above for a converging lens—that is, outer zones have a longer focal length than do inner ones. Accordingly, it is possible to combine a pair of suitably shaped converging and diverging lenses so as to correct, at the same time, chromatic aberration for two colors and spherical aberration for two zones.

Spherical aberration may also be corrected in a single lens by altering the lens shape from a simple spherical section in such a way as to give all zones of the lens the same focal length. Such an aspherical surface is
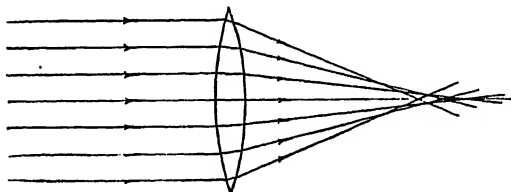
Fig. 16.   Spherical Aberration in a Biconvex Lens.

much more expensive to manufacture than a spherical surface. The importance of eliminating spherical aberration in spectrograph lenses is, however, so great that aspherical lenses are often used, especially in quartz spectrographs, where, as explained in the discussion of chromatic aberration, compound lenses present great difficulties.

The third type of image defect found in telescope lenses and, correspondingly, in collimator lenses, is coma. Coma, or the spherical aberration of rays which pass through the lens obliquely, results from the failure of the lens to form a sharp image of objects somewhat off the axis of the lens, that is, objects whose rays form a small angle with the optical axis. Because of this obliquity of incidence, the rays passing through the lower half of the lens strike the lens differently than do those passing through the upper half, and the resultant defective image is unsymmetrical. (See Fig. 17.) Whereas axial spherical aberration results in a symmetrical blur circle as the best obtainable image of a point, a comatic image of a point is a flare spot which may resemble a comet-tail or a butterfly. In a line image, blurred edges or even false companion lines are produced. Therefore, for best results, coma in a collimator lens must be removed or corrected, if possible. Since, as can be seen from Fig. 17, the comatic flare is reversed by reversing the curvature of the lenses, it is

possible even in a single lens to choose the two curvatures so as greatly to reduce the coma. A diaphragm placed in front of a lens can also greatly reduce coma by removing the rays which strike the lens surface most obliquely; these rays, as may be seen in Fig. 17, cause most of the coma.

It appears, then, that if a single lens is to be used as a collimator lens, the proper choice of curvatures, together with a stop, if necessary, will reduce the coma; spherical aberration may be removed by grinding the outer zones of the lens to an aspherical figure; chromatic aberration may
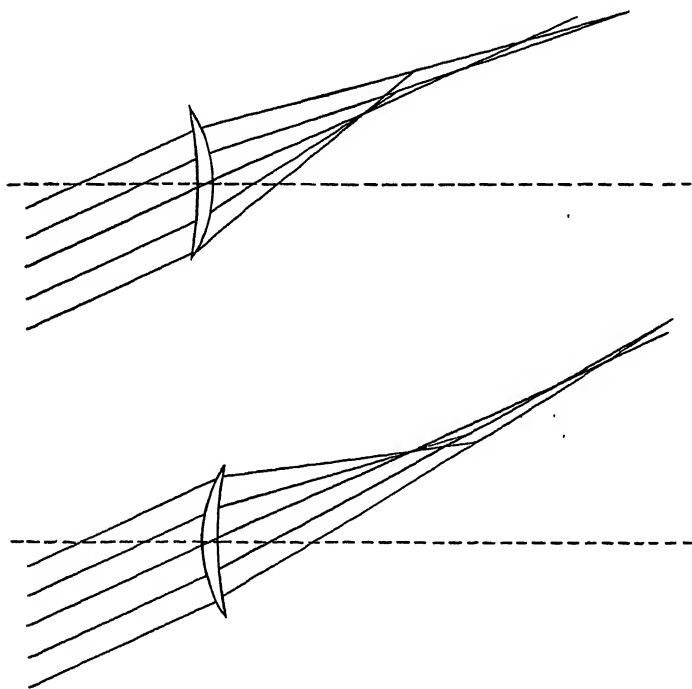
Fig. 17. Coma Produced by a Meniscus Lens in a Parallel Beam. Note that the coma is reversed by reversing the curvature of the lens in the two cases.

be taken care of by tilting the plate. If it is possible and feasible to use a compound lens in the collimator, the three aberrations in question can be corrected simultaneously. A proper choice of the relative strengths of the two lenses will give achromatism for two colors; a suitable "bending" of each lens, that is, distributing the necessary curvature between the two surfaces (which can be done without affecting the power of the lens), will permit the curvatures to be chosen so as to correct both coma and spherical aberration for one zone.

28. Prisms

The theory of the refraction of light by a prism, or prism system, has been discussed in detail by writers on geometrical optics.[10]   A treatment of the theory will not be undertaken here.   It may be pointed out, however, that a new type of image defect is introduced by the passage of a light bundle through a prism.   The result of this defect—astigmatism— is that a point image is not formed of a point source; rather, two image-lines are found at different distances from the optical system, perpendicular to each other and to the light bundle.   These so-called astigmatic image-lines occur also in the case of the oblique passage of light bundles through lenses and are illustrated in the discussion of the camera lens
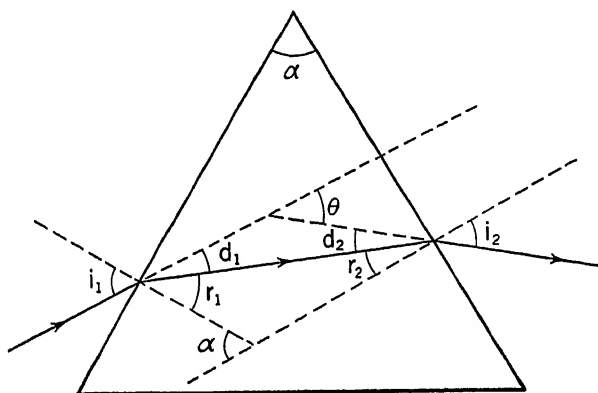
Fig. 18.   Path of a Ray Through a Principal Section of a Prism.

(Fig. 26, page 76).   If an object consists of vertical and horizontal lines, the vertical lines, as a result of astigmatism, appear to be imaged in the surface of one of the image-lines, while the horizontal lines are imaged in the surface of the other image-line.   Since, in spectroscopy, we are usually concerned with the imaging of vertical lines—slit images— astigmatism can be tolerated in a spectrograph.   Good slit images can be obtained by placing the photographic plate or eyepiece at the focal surface of the vertical image-line.   The theory shows, however, in the case of the prism, that the astigmatism is a minimum,   and the definition the best, if:

     1. The prism is traversed by parallel light.

     2. The slit is parallel to the prism edge.

     3. The light rays are parallel to a "principal section" of the prism, that is, a section perpendicular to the edge.

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[10] For example, J. P. C. Southall, *Principles and Methods of Geometrical Optics*, Ch. IV, New York: The Macmillan Company, 1913, and Kayser, H., *Handbuch der Spectroscopie*, Vol. I, Ch. III (written by H. Konen), Leipzig: S. Hirzel, 1900.

4. The rays pass through the prism symmetrically, that is, with equal refraction at each surface. The rays then pass at "minimum deviation" (see below).

These conditions cannot all be perfectly realized when the rays from light of a considerable wave-length range are studied simultaneously, and when a slit of finite length and a beam of finite aperture are used. It is desirable at least to approximate these conditions, however, and all prism spectrographs are built with that end in view. Some of the consequences of approximation will be noted later.

The path of a ray through a principal section of a prism of refracting angle A is shown in Fig. 18. The angular deviation produced in the ray by its passage through the prism is θ, and it is readily seen that

$$\alpha = r_1 + r_2 \text{ and } \theta = d_1 + d_2 = i_1 - r_1 + i_2 - r_2$$
$$= i_1 + i_2 - (r_1 + r_2)$$
$$= i_1 + i_2 - \alpha \qquad (24)$$

If the ray traverses the prism symmetrically, so that $i_1 = i_2$, and consequently $r_1 = r_2$, the deviation θ is less than that for any other angle of incidence.[11] The ray is called the *ray of minimum deviation*, and the prism is said to be set at minimum deviation. Since, as noted above in condition 4 for minimum astigmatism, the position of minimum deviation is favorable to the best image formation, spectrographs are ordinarily adjusted to or near this position. Accordingly, the discussions of prismatic dispersion and resolving power will be for the ray of minimum deviation.

29. Dispersion of a Prism

Since at minimum deviation, $i_1 = i_2$ and $r_1 = r_2$, Equation (24) becomes $\theta = 2i - \alpha$ and

$$i = \frac{\theta + \alpha}{2}$$

Also, since $A = r_1 + r_2 = 2r$,

$$r = \frac{\alpha}{2}$$

Snell's Law of Refraction may then be written,

$$n = \frac{\sin i}{\sin r} = \frac{\sin \dfrac{\theta + \alpha}{2}}{\sin \dfrac{\alpha}{2}} \qquad (25)$$

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[11] The Law of Minimum Deviation was known to Newton, and many proofs of the law have been given. Cf. the bibliography in Kayser's *Handbuch der Spectroscopie*, Vol. I, p. 258.

This equation is the basis of the method devised by Fraunhofer for the first accurate determinations of the index of refraction (see Sec. 4) from a measurement of the angles θ and α.

By differentiation of Equation (25),

$$\frac{dn}{d\theta} = \frac{\cos\dfrac{\theta + \alpha}{2}}{2\sin\dfrac{\alpha}{2}} \quad .$$

or

$$\frac{d\theta}{dn} = \frac{2\sin\dfrac{\alpha}{2}}{\cos\dfrac{\theta + \alpha}{2}} \tag{26}$$

But

$$\sin^2\frac{\theta + \alpha}{2} + \cos^2\frac{\theta + \alpha}{2} = 1, \text{ or } \cos\frac{\theta + \alpha}{2} = \sqrt{1 - \sin^2\frac{\theta + \alpha}{2}}$$

and by Equation (25),

$$\sin\frac{\theta + \alpha}{2} = n\sin\frac{\alpha}{2}$$

whence, Equation (26) becomes

$$\frac{d\theta}{dn} = \frac{2\sin\dfrac{\alpha}{2}}{\sqrt{1 - n^2\sin^2\dfrac{\alpha}{2}}} \quad . \tag{27}$$

While Equation (27) is strictly true only for small values of d, actually it is nearly true even for $d\theta$ as large as 8–10°.   Thus, we have

$$\Delta\theta = \Delta n\,\frac{2\sin\dfrac{\alpha}{2}}{\sqrt{1 - n^2\sin^2\dfrac{\alpha}{2}}}$$

To find the angular opening produced by a prism between two rays of wave length λ_1 and λ_2, for which the indices of refraction are, respectively, n_1 and n_2, $\Delta n = n_1 - n_2$, and n is replaced by the average

$$\bar{n} = \frac{n_1 + n_2}{2},$$

whence

$$\Delta\theta = (n_1 - n_2)\,\frac{2\sin\dfrac{\alpha}{2}}{\sqrt{1 - \bar{n}^2\sin^2\dfrac{\alpha}{2}}} \tag{28}$$

This equation is useful for calculating the length on the photographic plate of a given spectral region, since by Equation (2),

$$\Delta x = f\Delta\theta$$

The true angular dispersion $d\theta/d\lambda$ (see Sec. 16) may be obtained by use of the relation,

$$\frac{d\theta}{d\lambda} = \frac{d\theta}{dn} \cdot \frac{dn}{d\lambda} \tag{29}$$

$d\theta/dn$ is given by Equation (27). To obtain an analytical expression for $dn/d\lambda$, an equation is needed for the relation between λ and n. (A good approximation for $dn/d\lambda$ may be obtained from the slope of an n vs. λ graph.) A convenient equation for calculation, which is sufficiently good for small ranges, is the well-known interpolation formula of Hartmann,[12]

$$\lambda = \lambda_0 + \frac{C}{n - n_0} \tag{30}$$

whence

$$n = n_0 + \frac{C}{\lambda - \lambda_0}$$

and

$$\frac{dn}{d\lambda} = -\frac{C}{(\lambda - \lambda_0)^2} \tag{31}$$

Then

$$\frac{d\theta}{d\lambda} = \frac{2 \sin \frac{\alpha}{2}}{\sqrt{1 - n^2 \sin^2 \frac{\alpha}{2}}} \cdot \frac{-C}{(\lambda - \lambda_0)^2} \tag{32}$$

It is readily demonstrated that the dispersion of a train of several prisms, all adjusted for minimum deviation, is equal to the algebraic sum of the dispersions of the separate prisms.[13] Thus, for m identical prisms, Equation (32) becomes

$$\frac{d\theta}{d\lambda} = \frac{2m \sin \frac{\alpha}{2}}{\sqrt{1 - n^2 \sin^2 \frac{\alpha}{2}}} \cdot \frac{-C}{(\lambda - \lambda_0)^2} \tag{33}$$

To apply Equation (32) in finding the angular dispersion of a prism of angle A at any wave length λ, for which the index of refraction is n, the constants C and λ_0 must first be determined from Equation (30).

[12] J. Hartmann, *Astrophys. J.*, **8**, 218, 1898.
[13] J. P. C. Southall, *Principles and Methods of Geometrical Optics*, p. 488.

Since Hartmann's formula has three constants, C and λ_0 may be determined from the three simultaneous equations, obtained by substitution, in turn, of three values of λ and the corresponding known values of n.

For example, for a single 60° glass prism of dense flint, if

$$\lambda_1 = 4046.8A, \; n_1 = 1.69005$$
$$\lambda_2 = 4358.6A, \; n_2 = 1.68030$$
$$\lambda_3 = 4861.3A, \; n_3 = 1.66911$$

The constants of the Hartmann formula are:

$$\lambda_0 = 2034.57, \; C = 146.2336, \; n_0 = 1.61738$$

Whence, for $\lambda = 4358.6$,

$$\frac{dn}{d\lambda} = \frac{146.2336}{(4358.6 - 2034.6)^2} = 2.708 \times 10^{-5}$$

and

$$\frac{d\theta}{d\lambda} = \frac{2 \sin 30°}{\sqrt{1 - \frac{1}{4}(1.68030)^2}} \cdot 2.708 \times 10^{-5} = 4.9920 \times 10^{-5} \frac{\text{radians}}{\text{angstrom}}$$

30. Resolving Power of a Prism

The theoretical resolving power of a prism, $\lambda/\Delta\lambda$, at minimum deviation may be readily computed on the basis of the discussion of resolving
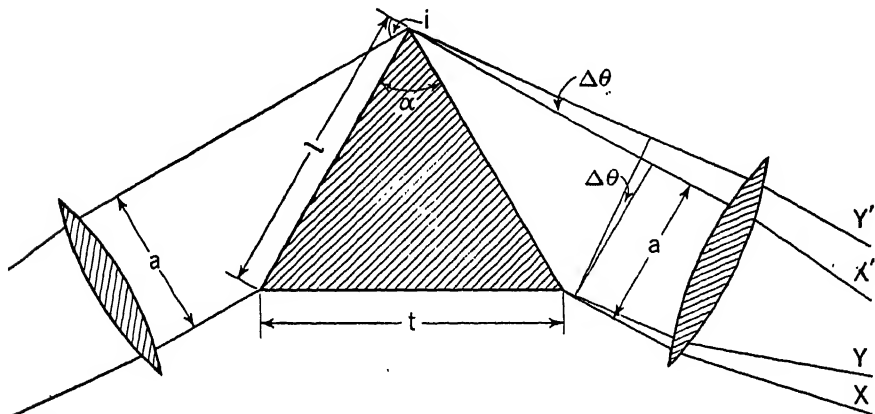
Fig. 19. **Resolving Power of a Prism.** Paths are shown of beams of two wave lengths which are just resolved.

power given in Section 17. Consider, as in that discussion, light from an infinitely narrow slit passing through a prism of rectangular aperture, dispersed in the cross-section view of Fig. 19 into two emergent beams xx' and yy' of wave lengths λ and $\lambda + \Delta\lambda$, respectively, such that their

images in the focal plane of the camera lens are just resolved. These emergent beams are separated, according to Equation (5), by an angle

$$\Delta\theta = \frac{\lambda}{BA} = \frac{\lambda}{a} \qquad (34)$$

(putting for BA, a, which is the beam width, or effective aperture, in this case).

Substituting the expression of Equation (34) for $\Delta\theta$ in Equation (6) for resolving power,

$$R = \frac{\lambda}{\Delta\theta} \cdot \frac{d\theta}{d\lambda} = a\frac{d\theta}{d\lambda}$$

or, by Equation (29), since

$$\frac{d\theta}{d\lambda} = \frac{d\theta}{dn} \cdot \frac{dn}{d\lambda}$$

$$R = a\frac{d\theta}{dn} \cdot \frac{dn}{d\lambda}$$

and since, by Equation (27),

$$\frac{d\theta}{dn} = \frac{2\sin\frac{\alpha}{2}}{\sqrt{1 - n^2\sin^2\frac{\alpha}{2}}} \quad \text{and also} \quad \sqrt{1 - n^2\sin^2\frac{\alpha}{2}} = \cos i,$$

$$R = \frac{2a\sin\frac{\alpha}{2}}{\cos i} \cdot \frac{dn}{d\lambda}$$

but, since from Fig. 19 $a = l\cos i$, and $2l\sin\frac{\alpha}{2} = t$,

$$R = t\frac{dn}{d\lambda} \qquad (35)$$

It will be noted that this expression for resolving power assumes that the entire prism face is used. If such is not the case, t, the thickness of the prism base, must be replaced by $(t - s)$, the effective thickness, where t and s are the thicknesses of the material through which the two extreme rays of the beam pass. Clearly, also, as in the case of dispersion, the resolving power of a train of prisms is equal to the algebraic sum of the resolving powers of the individual prisms. The resolving power depends on the effective thickness of the prism traversed, and thus several small prisms will have no greater resolving power than one large one of the same total effective thickness, while, as was pointed out on page 58 above, the dispersion of such a train of m prisms is m times that of a single prism.

Since the resolving power does not depend on the height of the prism, it is desirable, if the aperture of a prism spectrograph is to be diminished, to cut down the energy transmitted by reducing the height rather than the width of the beam. Thus the thickness of the glass traversed, and hence the resolving power, is maintained.

The resolving power of a prism may be readily calculated with the aid of the expression of Equation (31) for $dn/d\lambda$. Thus, for the glass used in the example on page 59, the resolving power at 4358A is:

$$R = t\frac{dn}{d\lambda} = 2.708 \times 10^{-5}t \quad (t \text{ in angstroms})$$
$$= 2708t \quad (t \text{ in cm})$$

In each case t is the effective thickness.

31. Curvature of Lines in Prismatic Spectra

It was pointed out (page 55) that one of the conditions for obtaining the best definition with a prism was that the light rays be parallel to a principal section of the prism. A point source or slit on the axis of the collimator lens fulfills this condition; with a slit of finite length, rays from slit points off the axis must traverse the prism at angles to the principal section which increase with the slit length. If this obliquity is large, the definition of the line ends will be adversely affected. Furthermore, these oblique rays traverse greater prism thicknesses than do parallel rays—in effect, they are dispersed by prisms of greater angles—and are accordingly deviated more. Since the light from the slit ends is deviated more than that from the center, the result is that the slit images are curved. The theory of this line curvature is discussed in detail by Kayser.[14] The curve is approximately a parabola; the radius of curvature at the vertex is given by

$$r = \frac{n^2 f}{2(n^2 - 1)} \tan i \qquad (36)$$

(f = focal length of camera lens, i = angle of incidence)

It will be seen that r is less, that is, the line is more curved, as f decreases or n increases. Since the index of refraction increases toward the violet, the lines become more curved at this end of the spectrum.

Line curvature is troublesome when two adjacent spectra are to be compared, or when one is to be used as a "comparison spectrum" in the calibration of the other. (See page 226.) Care must be taken to see that the two spectra are measured at the corresponding points or that a correction for curvature is applied. Special difficulty arises when the lines are to be received on a linear thermopile, as in infrared spectra,

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[14] H. Kayser, *Handbuch der Spectroscopie*, Vol. I, p. 319.

and particularly in the case of instruments of short focal length. A similar situation has been met by Randall and Firestone[15] in their large-aperture grating spectrometer by the use of an exit slit of variable curvature, which can be adjusted to compensate for the line curvature in the spectral region under observation. Curved entrance slits have also been employed.

32. Magnification by a Prism

In spectrographs, prisms are almost invariably used at or near the position of minimum deviation. The rays traverse the prism symmetrically, and hence the entering and emergent beams are of the same width. With camera and collimator lenses of equal focal length, the slit and its image, neglecting diffraction, will have the same width; there is no magnification by the prism. If, however, the incident and emergent angles are not equal, the corresponding beams are of different widths, and so are the slit and its image. The resulting magnification factor is, in the terminology of Fig. 18,

$$\frac{\cos i_1 \cos r_2}{\cos r_1 \cos i_2},$$

and may vary from 0 for grazing incidence ($i_1 = 90°$), to ∞ for grazing emergence ($i_2 = 90°$).[16] The dispersion of the spectrum will be altered in the same ratio as the line width, so that there is no gain or loss in resolution by prism magnification. The device is sometimes used, as in the half-prism (page 71), to permit the use of smaller prisms with particular lenses.

33. Size of Prism Faces

Although requirements of economy often necessitate a smaller prism, the prism face should, for maximum illumination, be of such dimensions that, without loss of light or waste of prism material, it will accept the full beam of rays from the collimator. The circle of the collimator lens periphery should be just inscribed in the square formed by the projection of the prism face on the lens. The height of the prism should then be the same as the diameter of the collimator lens. The length of the prism face must, however, be considerably greater than its height. Referring to Fig. 19, it is seen that the length l of the face is related to the diameter of the collimator a by the relation

$$a = l \sin (90 - i) = l \cos i$$

[15] H. M. Randall and F. A. Firestone, *Rev. Sci. Inst.*, **9**, 404, 1938.
[16] H. Kayser, *Handbuch der Spectroscopie*, Vol. I, p. 277.

and, since, as shown on page 57,

$$\cos i = \sqrt{1 - n^2 \sin^2 \frac{\alpha}{2}}$$

$$a = l \sqrt{1 - n^2 \sin^2 \frac{\alpha}{2}} \qquad (37)$$

For 60° prisms, which are ordinarily used,

$$a = l \sqrt{1 - \frac{n^2}{4}}$$

Since the beam spreads by dispersion in traversing the prism, the emergent face must be slightly longer than the minimum entrance face. In general, it does not pay to construct prisms with unequal faces, and the actual prism is made enough larger than required by Equation (37) so that it will pass the entire beam. This additional length is readily computed by tracing the ray of shortest wave length through the prism base with the help of Snell's law and simple trigonometrical relations. The long wave-length ray falls outside the ray of minimum deviation only at the tip of the prism, and so does not require a longer second face.

The broadening of the beam in its passage through a prism requires that the second prism in a prism train be larger than the first, and succeeding prisms must be still larger if each prism is to be of the minimum size. Similarly, the camera lens must be of larger diameter than the collimator lens, if each is to pass the full beam through a minimum aperture. Since the cost of prisms and lenses rises nearly proportionately to their area, or even more rapidly in larger sizes, it is ordinarily worth while to take advantage of the possibility of using optics of smaller aperture in the first units of a train than are needed in the later elements.

34. Prism Materials

The ideal prism material should be transparent over a wide wavelength range, isotropic, available in large homogeneous pieces, capable of taking an excellent optical polish on its surfaces, resistant to atmospheric exposure and laboratory fumes, and have relatively large angular dispersion $(d\theta/d\lambda)$ and a relatively small temperature coefficient of index of refraction (dn/dt). Optical media satisfying all these requirements in all desired wave-length regions are not available, and some compromises must often be accepted.

In the visible region, the possibilities are by far the best. In the first rank, of course, come the wide varieties of optical glass, which is generally preferred for use in the visible region because of its relative cheapness. In the ultraviolet, the lighter crown glasses are transparent to somewhat beyond the visible limits, while a special ultraviolet transmitting glass,

uviol, is transparent in prism thicknesses to about 3000A. For use in the visible region, when the range need not be extended much beyond the visible violet, flint glass is usually preferred because of its much greater dispersion. The heavier flint glasses, however, are useful to wave lengths little, if any, shorter than 4000A.

For purposes of comparison, the accompanying table gives data on some typical glasses. The second column gives the index of refraction for the D ray (5893A); the third column, the mean dispersion, or difference, of the indices for the C and F rays (6563A and 4861A, respectively); and the fourth column, the value of $d\theta/d\lambda$ calculated for a 60° prism for the wave length 5893A. The angular dispersion of these glasses, of course, increases largely toward the violet as the limit of transparency is approached. Data on other glasses may be found in the various handbooks of physical constants.

Glass Type	n_D	$n_F - n_C$	$(d\theta/d\lambda)_D$ in radians/angstrom[a]
Uviol crown....	1.5035	.0078	$.616 \times 10^{-5}$
Silicate crown..	1.5271	.0087	$.700 \times 10^{-5}$
Light flint......	1.5804	.0139	1.144×10^{-5}
Dense flint.....	1.6555	.0190	1.703×10^{-5}

[a] $d\theta/d\lambda$ is calculated by Eq. 33 for the rays C, D, and F.

Liquid prisms have been used to some extent in the visible region and also in the ultraviolet. The liquids are enclosed in a hollow prism with plane parallel sides, or in a tube between two glass prisms. The liquid prism has the great advantages of relative cheapness, especially in large sizes, of uniformity and homogeneity, and of a wide range of materials and dispersions. The great disadvantage of liquids is their uniformly high temperature coefficient of dispersion, which is usually of the order of from ten to one hundred times that of glass. Temperature gradients in the liquid give rise to inhomogeneities in dispersion and to convection currents, and lead to changes in dispersion and to loss of resolution. Accordingly, much closer temperature control is required than for solid media. In spite of this difficulty, the large dispersions obtainable with liquids, together with their other advantages, justify the use of liquid prisms in special applications.

The liquids which have been most used in prisms are water, carbon bisulphide, monobromonaphthalene, ethyl cinnamate, and the water solution of barium mercuric bromide. The following table gives some of the optical characteristics of these liquids, including the index for the D ray, the mean dispersion, the angular dispersion for a 60° prism at the D ray, and the mean temperature coefficient of index of refraction (dn/dt) for the visible region. It may be noted that dn/dt for the ordi-

nary glasses for the visible region, at room temperature, is generally in the range from 1×10^{-6} to 5×10^{-6}.[17]

Liquid	n_D at 20°	$n_F - n_C$	$(d\theta/d\lambda)_D$	$(dn/dt)_D$
Water........................	1.3330	.0060	$.416 \times 10^{-5}$	$- .8 \times 10^{-4}$
Carbon bisulphide..............	1.6276	.0341	2.885×10^{-5}	$- .8 \times 10^{-4}$
Monobromonaphthalene.........	1.6576	.0325	2.501×10^{-5}	-4.5×10^{-4}
Ethyl cinnamate...............	1.5604	.0285	2.212×10^{-5}	-3.4×10^{-4}
Aqueous solution of barium mercuric bromide[a]...............	1.6100	.0274		

[a] These figures are for a solution with the same n_D as barium crown glass. No data are given on the other constants. (J. Duclaux and G. Ahier, *Revue d'Optique*, **17**, 417, 1938.)

In spite of its low dispersion, water has been used to a considerable extent in liquid prisms. Its low temperature coefficient of index of refraction makes it less troublesome to use than other liquids, and its great transparency in the ultraviolet gives it importance in the region near 2000A. Thus, Duclaux and Jeantet[18] have pointed out not only that water is highly transparent in the region 2100A to 1800A, but also that the mean dispersion of water in the region 1990A to 1862A is almost 20 per cent greater than that of quartz (.0277 as against .0233). Furthermore, the smaller index of refraction of water permits larger prism angles for equal reflection losses (70° as against 60°) with consequent gain in angular dispersion. Finally, large homogeneous quartz crystals are difficult to find and are likely to fail in transparency below 2200A; and for that reason, also, water cannot be disregarded as a dispersing medium in this region.

Carbon bisulphide, because of its high dispersion, was proposed very early as a dispersing medium.[19] It is transparent from 3500A to about 3μ, with further transmission regions between 2400A and 2800A and below 1850A,[20] and between 24 and 60μ in the infrared.[21] There are, however, numerous disadvantages in the use of carbon bisulphide. It is volatile (boiling point, 46°C), and the vapor is inflammable, forms an explosive mixture with air, and ignites at a low temperature (232°C). The liquid is decomposed by ultraviolet light of wave lengths shorter than 3660A, with deposition of sulphur.[22] Finally, the temperature coefficient of index of refraction is one of the highest, so that the prism

[17] C. Pulfrich, *Ann. d. Phys.*, **45**, 238, 1892; J. W. Gifford, *Proc. Roy. Soc.*, **91A**, 319, 1915.
[18] J. Duclaux and P. Jeantet, *Revue d'Optique*, **2**, 384, 1923.
[19] D. Brewster, *Edinburgh Trans.*, **8**, 285, 1814.
[20] E. Flatow, *Ann. d. Phys.*, **12**, 91, 1903.
[21] H. Rubens and E. Aschkinass, *Ann. d. Phys.*, **64**, 602, 1898, and **65**, 241, 1898.
[22] G. Bruhat and M. Pauthenier, *Comp. Rend.*, **178**, 1536, 1924.

temperature must be controlled to about .01°C if the resolving power is not to suffer. As a result of these drawbacks, and especially of the last, carbon bisulphide is little used in liquid prisms, except for demonstration purposes or for very brief exposures.

Data have been given on monobromonaphthalene by J. W. Bruhl[23] and on ethyl cinnamate by Wernicke.[24] These liquids have slightly less dispersion than carbon disulphide but less than half the temperature coefficient of index of refraction. They are usable throughout the visible region, have relatively high boiling points (279° and 271°C, respectively), and are stable. They have been proposed recently, chiefly for use in instruments with high illumination, some examples of which will be described later.

The use of aqueous solutions as dispersing media has been proposed by Jeantet and Duclaux.[25] Duclaux and Ahier (*loc. cit.*) have described a direct-vision prism utilizing barium crown glass and an aqueous solution of barium mercuric bromide, of proper strength to have the same index of refraction for the D lines as the glass has. The dispersion of the solution (see preceding table) is about the same as that of ethyl cinnamate. The solution is claimed to have a much smaller thermal expansion and a greater stability than the cinnamate. No data are given on these points by the authors. Barium mercuric bromide is usable only in the visible region, as its absorption region begins at 3800A.

Numerous crystals have been used for prism materials, especially for application in the ultraviolet or infrared regions, where glass is not transparent. Some of the optical characteristics of the most-used crystals are given in the following table:

Formula	Material	n_D	n_F-n_C	$(d\theta/d\lambda)_D$	$(dn/dt)_D$
KI........	Potassium Iodide	1.6634	.0287	2.881×10^{-5}*	$-5 \quad \times 10^{-5}$**
KBr......	Potassium Bromide	1.5581	.0177	1.449×10^{-5}*	-3.6×10^{-5}**
LiF.......	Lithium Fluoride	1.39177	.0040	$.286 \times 10^{-5}$*	-2.3×10^{-5}‡
CaF₂......	Fluorite	1.43385	.0045	$.333 \times 10^{-5}$†	-1.0×10^{-5}§
SiO₂......	Crystalline Quartz	1.54426	.0078	$.628 \times 10^{-5}$†	$- .5 \times 10^{-5}$
SiO₂......	Fused Quartz	1.45848	.0067	$.517 \times 10^{-5}$	$- .6 \times 10^{-5}$
NaCl.....	Rock Salt	1.54431	.0127	$.938 \times 10^{-5}$†	-3.7×10^{-5}
KCl.......	Sylvite	1.49038	.0113	$.729 \times 10^{-5}$†	-3.6×10^{-5}

* Data from F. H. Perrin, *J. Opt. Soc. Am.*, **28**, 86, 1938.
† *Dictionary of Applied Physics*, IV, 136.
** K. Korth, *Zeits. f. Phys.*, **84**, 677, 1933; J. W. Forrest, *J. Opt. Soc. Am.*, **32**, 382, 1942.
‡ H. W. Hohls, *Ann. d. Phys.*, **29**, 433, 1937.
§ Ordinary ray.

23 J. W. Bruhl, *Zeits. Phys. Chem.*, **22**, 373, 1897.
24 W. Wernicke, *Zeits. f. Instrkde.*, **1**, 353, 1881.
25 P. Jeantet and J. Duclaux, *Revue d'Optique*, **14**, 345, 1935.

The first three of these crystals are grown artificially (see page 279); the others occur naturally. Fused quartz is prepared from the natural material. Of these materials only crystalline quartz is used to any extent in visible spectroscopy. The others find application in the ultraviolet and infrared regions.

Lithium fluoride, fluorite, and crystalline and fused quartz are especially valuable in the ultraviolet, being transparent to about 1200A, 1200A, and 1850A, respectively. Artificial lithium fluoride is as yet not readily available commercially. Fluorite is rarely to be had in pieces over an inch in diameter. Furthermore, the small dispersion of these materials renders them inferior to quartz in the region above 2000A. They are, however, used, as noted earlier (page 52), in combination with quartz for achromatic lenses for the ultraviolet region, and in small vacuum-prism spectrographs for use below 2000A, where their dispersion becomes higher as their transmission limit is approached. Quartz is one of the commonest minerals but is found in only a few localities in crystals of large size and optical quality. It is, however, to be had in reasonable quantity in crystals large enough to yield prisms of from six to eight centimeters in height, and is, after glass, the most widely used spectrographic material.

Quartz is a doubly refracting crystal. A beam of unpolarized light incident on a doubly refracting crystal is divided into two perpendicularly polarized beams, one of which, the ordinary ray, obeys Snell's law, while the other, or extraordinary ray, is refracted at an angle, the relation of which to the angle of incidence depends on the angle of incidence in a more complicated way. The extraordinary ray thus has an index of refraction different from the ordinary ray; and since the index of refraction is the ratio of ray velocity in air to that in the medium, the extraordinary ray travels with a different velocity in the quartz from that of the ordinary ray, its velocity depending on the direction of travel. This phenomenon of double refraction leads to the formation of two images whose separation depends on the amount of double refraction. However, in one direction—the optic axis—the two rays travel with the same velocity, and the effect of double refraction disappears. Lenses are cut from crystal quartz, therefore, with the optic axis of the crystal parallel to the lens axis. All rays pass through the lens at angles to the optic axis small enough so that the birefringent effect, which is rather small in quartz, is negligible. Crystal quartz prisms are cut with the optic axis in a principal plane and parallel to the prism base. Rays at minimum deviation then suffer no double refraction, and that for other rays is not appreciable.

In addition to double refraction, quartz also possesses the property of rotating the plane of polarization of a beam of plane-polarized light. Since a birefringent crystal separates an unpolarized beam of light into

two beams, plane-polarized at right angles, this rotational effect will appear even in a beam parallel to the optic axis. According to Fresnel, the plane-polarized beam is resolved into two beams circularly polarized in opposite directions and traveling with different velocities, so that the amount of the effect depends on the distance traversed in the crystal. The result of the different beam velocities—equivalent, as noted above, to a difference of refractive index—is to produce a double image even in rays parallel to the optic axis. Fortunately, however, quartz occurs in two crystal forms, called right-handed and left-handed because the two forms produce in a plane-polarized beam of light a rotation of the plane of polarization in a clockwise and counterclockwise sense, respectively. The rotational effect in the spectrograph lenses may then be avoided by making the camera lens of one variety of quartz and the collimator lens of the other. The prism may be made, after a method due to Cornu, by building up a 60° prism from two 30° prisms, one from each variety of quartz. The rotational effect may likewise be avoided, as in the Littrow-type spectrograph, by the use of a single lens and a 30° prism, backed by a mirror. The light from the slit collimated by the lens and passing through the prism experiences the rotatory effect, but after reflection by the mirror it again traverses the prism and is then brought to a focus by the lens. The second passage through the lens and prism, after the mirror reflection, introduces a compensating rotatory effect to neutralize that of the first passage.

As noted above, quartz is the outstanding material for spectrographic use in the ultraviolet region between approximately 2000A and 3800A. Not all quartz is equally transparent at the lower end of this range, and prisms for use between 2100A and 1900A must ordinarily be especially selected. Quartz is perfectly transparent throughout the visible region, and, although its dispersion in this region is much less than that of glass, "universal" quartz spectrographs are often designed for use both in the ultraviolet and in the visible parts of the spectrum. The transparency of quartz also extends to about 3.5μ, and quartz is often chosen for work in this shorter infrared region.

Fused quartz has been prepared in large pieces in the United States, by the General Electric Company, and in Germany. At its best, it is as transparent as crystalline quartz. As will be seen from the table, its indices of refraction and dispersion are somewhat less than those of the crystal. Because of the high melting point of quartz, it has as yet not been possible to melt it thoroughly enough to get rid of all bubbles and inhomogeneities and so to produce material of the first optical quality. If it should later become possible to produce optically excellent fused quartz in large pieces, this material would be of spectroscopic importance because its isotropism would avoid the difficulties due to the double-refraction and rotational effects in quartz. At present, however, it is

used optically chiefly for windows on furnaces and discharge tubes and for lenses where the highest quality is not essential or where the size of the piece is not great.[26]

The other crystalline materials used are various alkali halides, all of which have wide ranges of transparency in the ultraviolet and infrared, as well as throughout the visible. These crystals are all cubical in form and so behave optically as if isotropic; that is, they are free from birefringence. The alkali halides are all, like salt, more or less deliquescent and must be protected from moisture. Accordingly, in the case of prism spectrographs, the prism is usually kept at a higher temperature than the surrounding air by an electric heater or gas flame, or the spectrograph is placed in an enclosure which can be dried or evacuated.

The regions of transmission of the crystalline materials are:[27]

Potassium iodide	2500A to 31μ
Potassium bromide	2100A to 28μ
Lithium fluoride	1200A to 7μ
Fluorite	1200A to 9μ
Crystalline and fused quartz	1850A to 3.5μ
Rock salt	2000A to 17μ
Sylvite	2000A to 21μ*

* Except for narrow absorption bands at 3.2μ and 7.1μ.

These limits are, of course, only approximate. At the red end they are the points at which the transmission of a 2-mm thickness of the material falls to about 50 per cent.

Where a selection of materials is possible in the infrared, it is usually best to choose for a particular region the crystal with long wave-length transmission limit just above the region. Since the dispersion increases rapidly as the limit of transparency is approached, this choice will ordinarily give the best dispersion and the best resolving power. The following table gives the most suitable prism materials for different parts

Region	Material	Least $\Delta\lambda$
Visible to 3.5μ	Quartz	2A
3μ to 9μ	Fluorite	8A
8μ to 16μ	Rocksalt	30A
15μ to 20μ	Sylvite	50A
19μ to 28μ	Potassium Bromide	70A

[26] L. W. Tilton and A. Q. Tool, *Bur. of Stand. J. of R.*, **3**, 619, 1929, conclude that the use of fused quartz is feasible in small optical parts provided the optical path does not greatly exceed a centimeter.

[27] *Dict. App. Phy.*, IV, p. 136; Z. Gyulai, *Zeits. f. Phys.*, **46**, 80, 1927. M. Czerny and H. Röder, *Ergebnisse d. Exakten Naturwiss*, V 17, p. 97.

of the infrared region,[28] and the approximate value of the smallest $d\lambda$, which is theoretically resolvable in each region by a prism of 5-cm base.[29]

35. Prism Types and Systems

Since prisms are almost always used at or near the position of minimum deviation, and since it is generally found best to use them at or near unit magnification—with equal incident and emergent angles—the most common prism systems are based upon the isosceles prism. The best choice of prism angles follows from a consideration of reflection losses and is dependent upon the index of refraction (see page 111). However, for most materials, a 60° prism angle is near the optimum, and equilateral prisms are most common.

In the case of crystalline quartz, as pointed out above (pages 67–68), the 60° prism is built up out of two 30° prisms—one of right-handed and the other of left-handed quartz. The two prisms should be in contact to prevent the reflection losses that would otherwise occur at the two quartz-air interfaces. If they are to be cemented together, a material that has an adequate range of transparency must be used. For use in the ultraviolet, such cements are not available. It was formerly customary to obtain an optical contact by placing a little water, alcohol, or preferably glycerine between the two prisms. None of these materials is wholly satisfactory, because they are not permanent and do not form a rigid joint. More recently it has been found that if two surfaces are optically flat to within a fraction of a wave length of light, they can be slid one over the other into an "optical contact" which is so good that they cannot be pulled apart.[30] To separate them, it is necessary to drive them apart from the side. Most Cornu prisms are now joined in this manner.

The 30° prism, or half-prism, is found in autocollimation or Littrow-type spectrographs. Here the light is reflected from the back surface of the prism and traverses the prism twice, with an effect equivalent to that of a single 60° prism. For use in the visible region the back surface is silvered, but, because of the poor reflecting power of silver in the ultraviolet, a mercury tin amalgam with better ultraviolet reflection has been used for that region. More recently, evaporated films of aluminum have been preferred because of their great permanence and high ultraviolet reflection.[31]

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[28] G. B. B. M. Sutherland, *Infra-red and Raman Spectra*, p. 5, London: Methuen, 1935.

[29] From Czerny and Röder, *loc. cit.;* the least $\Delta\lambda$, which is nearly constant for any material throughout each region, is given, rather than $\Delta\nu$, which is inversely proportional to λ.

[30] Cf. discussion of optical contact by Lord Rayleigh, *Proc. Roy. Soc.*, **156A**, 326, 1936.

[31] R. C. Williams and G. B. Sabine, *Astrophys. J.*, **77**, 316, 1933; J. Strong, *ibid.*, **83**, 401, 1936.

Two half-prisms are sometimes used with their long faces toward one another (Fig. 20). This arrangement is often credited to Thollon,[32] although it was described earlier by C. A. Young.[33] In the figure, the symmetrical path of a ray at minimum deviation is shown. It will be seen that if one prism, say A, and its associated collimator lens are fixed, while the other prism and lens rotate together about an axis at C, the ray at minimum deviation will always pass through the system symmetrically. The same effect can be attained if the two prism points, A and B, are in contact and this common point is used as the axis.

The Young-Thollon arrangement is often used in monochromators. In some applications of this prism arrangement, the collimator and telescope arms are fixed and both prisms rotate so as to bring different
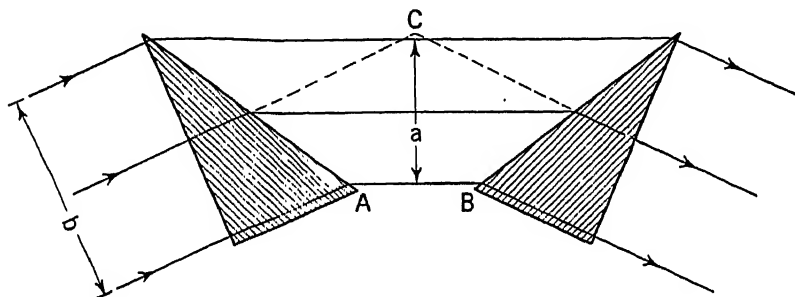
Fig. 20. The Young-Thollon Half-Prism Arrangement. Passage of a beam at minimum deviation is shown.

wave lengths into the field of view. In general, of course, only one wave length will pass through the system at minimum deviation.

An important advantage of the Young-Thollon arrangement follows from the fact that the beam b (Fig. 20) is much wider than the beam a. The magnitude of the effect may be calculated at once from Equation (37), which, for the ray at minimum deviation, gives the relation between length of prism face l and width of beam a as

$$a = l \sqrt{1 - n^2 \sin^2 \frac{\alpha}{2}} \tag{37}$$

In this case $\alpha/2$ will be the angle of the half-prism. It will be seen that

$$b = l \cos \frac{\alpha}{2}$$

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[32] L. Thollon, *Comp. Rend.*, **86**, 595, 1878.
[33] C. A. Young, *J. Frank. Inst.*, **62**, 348, 1871.

Hence,

$$\frac{b}{a} = \frac{\cos\frac{\alpha}{2}}{\sqrt{1 - n^2 \sin^2\frac{\alpha}{2}}}$$

For a 30° half-prism of index $n = 1.60$, $b/a = 1.44$.

In the conventional arrangement the beam a fixes the necessary aperture of collimator and telescope lenses, while in the half-prism arrangement b is the corresponding aperture. It is apparent, then, that with lenses of the same diameter or light-gathering power, the use of the half-prisms permits the use of smaller prisms. There will, of course, be a loss of resolving power, since this depends upon the thickness of the prism base. On the other hand, by reversing the half-prisms and employing them with the long face toward the lenses, the beam may be decreased
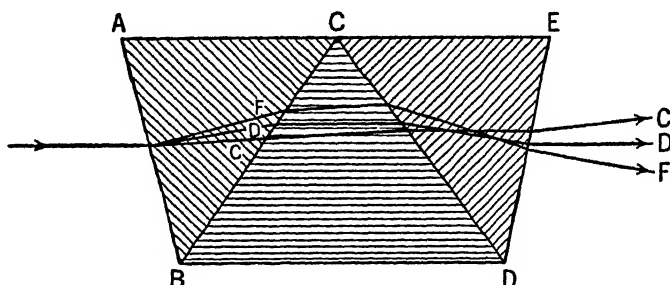
Fig. 21.   The Amici Prism.   The central, D, ray enters and leaves parallel to the base. The C and F rays are deviated and dispersed.

in aperture—an advantage if additional prisms are to be inserted in a train between the half-prisms, since the intermediate prisms may then be smaller.

Of the various forms of compound prisms made by cementing together two or more prisms of different materials the most important types today are the direct-vision arrangements, which give dispersion without deviation. In the form due to Amici[34] (Fig. 21), prisms ABC and CDE, of crown glass of a low ratio of dispersion to index of refraction, are combined with a prism BCD, of flint glass of a high ratio of dispersion to index. These systems are sometimes built up of five or seven prisms. Details of the design of direct-vision systems will be found in texts on geometrical optics.[35] Since in this type of prism the dispersion of the crown glass prisms opposes that of the flint glass prism, the dispersion and resolving power of the system are not great. Amici prisms are chiefly used in pocket and portable instruments for direct observation.

[34] G. B. Amici, *Museo Fiorentino*, 1, 1, 1860.
[35] For example, Southall, p. 491.

It was observed by Zenger[36] that the choice of two materials with the same index of refraction for a ray in the middle of the region used, but with different dispersions, makes possible the construction of a direct-vision prism in the form of a parallelopiped (Fig. 22). Because of the normal incidence at the first surface and the small incident angles at emergence, the reflection losses are much smaller than they are with the large angles met with in single or Amici prisms. The requirement of equal index for the central ray usually means that the second prism utilizes a liquid as the refracting medium. This prism is then subject to the disadvantages of liquid prisms previously discussed.
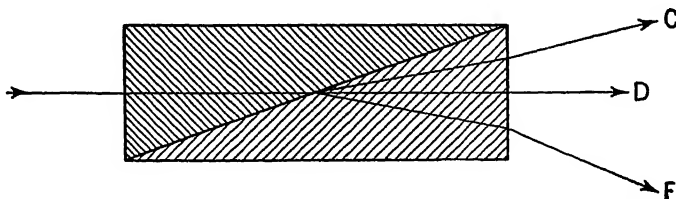
Fig. 22. The Zenger Prism. The central, *D*, ray is undeviated. The *C* and *F* rays are deviated and dispersed.
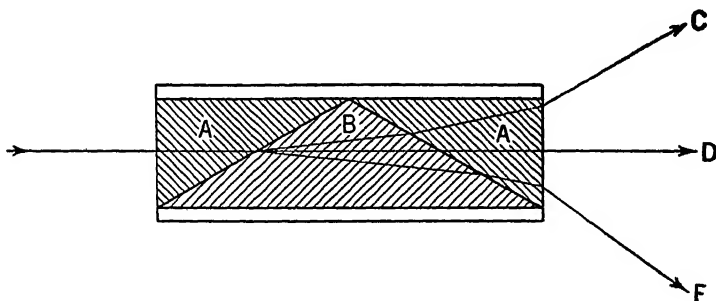
Fig. 23. The Wernicke Prism. This arrangement is essentially two Zenger prisms, back to back.

The compound, direct-vision prism using a liquid, in a form first described by Wernicke,[37] has recently been proposed again because it combines high light transmission with large dispersion. It will be seen from Fig. 23 that the Wernicke form is essentially two Zenger prisms placed back to back. In a prism of this type, Duclaux and Ahier[38] used barium crown for prisms *AA*, and a concentrated solution of barium mercuric bromide in *B*. Because of the high dispersion of this liquid and because of the large angle possible in prism *B* (about 103°), the angular dispersion is reported to be as large as that of two heavy flint-

[36] K. W. Zenger, *Zeits. f. Instrkde.*, **1**, 263, 1881.
[37] W. Wernicke, *Zeits. f. Instrkde.*, **1**, 355, 1881.
[38] J. Duclaux and G. Ahier, *Revue d'Optique*, **17**, 417, 1939.

glass prisms of index 1.72. The light transmission of the two flint prisms would be about 65 per cent, while the losses in the compound prism would be almost wholly at the plane ends and the transmission should exceed 90 per cent (see Sec. 43). In each case absorption losses are not considered.

By making the angles of the faces of the A prisms slightly less than 90°, Duclaux and Ahier, in a second design, were able to make the angle of prism B still greater (about 160°). They report that the angular dispersion is as much as that of six prisms of heavy flint glass, with at least as good transmission.

The firm of Adam Hilger offers a prism of the Wernicke type with perpendicular ends and with ethyl cinnamate as the liquid. The angular
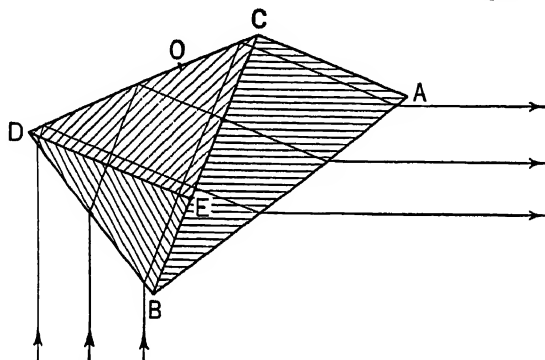
Fig. 24. The Pellin-Broca Prism. This prism is equivalent to two 30° prisms, ABC and BED, and one 45° prism, DEC, but is made in one piece. The beam shown, entering at minimum deviation, emerges at 90° deviation to its entrance direction.

dispersion at 4360A is given as 11.3×10^{-5} radians/angstrom. For a 60° glass prism of dense flint, it would be approximately 1.7×10^{-5}. It should be noted that because of the effect of the thick end prisms, this type of liquid prism is better insulated thermally than the conventional 60° type enclosed in thin glass plates. An additional advantage of this prism for such purposes as the study of Raman spectra is the fact that the dispersed light is almost completely unpolarized. In single prisms of the usual type, the light is partly plane-polarized because of the large angle of incidence (see page 111).

A prism which may be thought of as a compound prism, although most often made in one piece, is the four-sided prism (Fig. 24) in which the light beam undergoes two refractions, at the surfaces AB and BD, and a total reflection at the surface CD. It was first pointed out by Abbe[39] that this system permitted dispersion with a constant deviation for any wave length. In the Pellin-Broca form[40] shown, the arrange-

[39] Ernst Abbe, *Gesammelte Abhandlungen*, Vol. I, p. 1. Jena: Fischer, 1904.
[40] P. Pellin and A. Broca, *Jour. de Physique*, **8**, 314, 1899.

ment is equivalent to two 30° refracting half-prisms combined with a totally reflecting right-angle prism. The two refractions compensate for each other, and the deviation of the beam is the 90° change in direction introduced by the total reflection. The use of this prism permits the construction of an instrument with a collimator and telescope or camera fixed at 90° deviation. Different wave lengths are brought into the field of view by rotating the prism, preferably about the point O, which is the intersection of the face CD and the bisector of the angle at B.[41] This type of prism is frequently seen in monochromators and instruments for visual observation.

Another prism arrangement giving constant deviation, frequently seen in infrared spectroscopes, is shown in Fig. 25. First described by Fuchs,[42] this system is commonly attributed to Wadsworth,[43] who
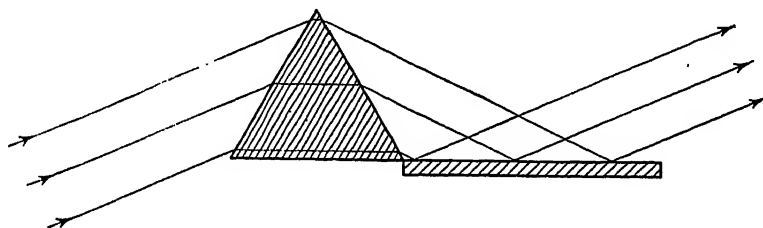
Fig. 25. The Wadsworth Prism-Mirror Arrangement. The beam enters the prism at minimum deviation and emerges displaced but not deviated from its original direction.

described it along with several other prism and mirror combinations giving constant deviation. The beam, after passing through the prism (Fig. 25), is reflected at the metallic mirror, which is on the extended line of the prism base. It will be observed that at minimum deviation, where the angles of incidence and emergence are equal, the effect of the reflection is to make the final path of the ray parallel to its original direction. The effect, then, is that of a direct-vision prism, but, unlike the Amici prism arrangement, it utilizes the full dispersion of the 60° prism. A disadvantage is the loss by reflection at the mirror surface. In the infrared region, where the arrangement is most often seen, high reflecting powers are easier to attain than in the visible and ultraviolet regions.

36. The Camera Lens

The camera or telescope lens has to bring to a focus the beams of light of various wave lengths emerging from the prism so as to form images of the slit. Since, as was pointed out in the discussion of prisms,

[41] W. E. Forsythe, *Astrophys. J.*, **45**, 278, 1917.
[42] Fr. Fuchs, *Zeits. f. Instrkde.*, **1**, 349, 1881.
[43] F. L. O. Wadsworth, *Astrophys. J.*, **1**, 232, 1895.

the various wave lengths emerge from the prism at different angles, these slit images form a spectrum of greater or less length in the focal plane. In the ideal case, the collimator lens renders the beams of all wave lengths parallel, or, in other words, makes the slit appear to be at an infinite distance. The camera lens thus has to form an extended image of a very distant source. Consequently, part of the slit images are formed at a considerable distance from the optic axis, and at such distances, or angular fields, new image defects appear which are not found in the collimator lens, dealing, as it does, only with images near the axis.
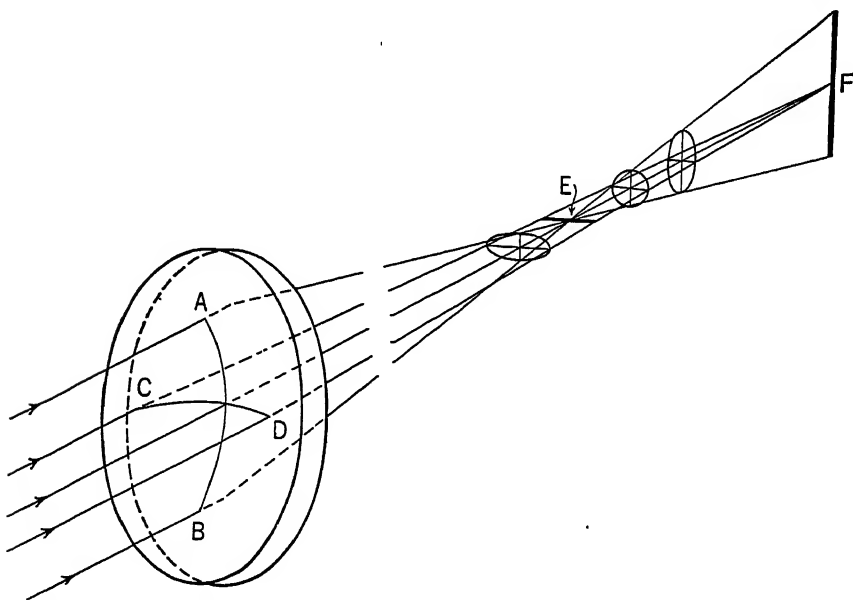
Fig. 26.   Astigmatism in a Lens Free from Spherical Aberration and Coma.

The most important new defects are astigmatism and curvature of the image. In the discussion of prisms, astigmatism has been referred to as the imaging of a point, not as a point, but as two mutually perpendicular image lines at different distances from the lens.[44] It arises from the dissymmetry introduced in a beam by oblique passage through a lens, and may still be found in lenses even after spherical aberration and coma have been removed. Pure astigmatism is illustrated in Fig. 26. Spherical aberration is absent, as is shown by the fact that rays in the vertical plane AB at different distances from the axis come to a focus at the same point E. However, rays in the horizontal plane CD are

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[44] *Astigmatism* is used here, as is usual in the discussion of lens errors, to denote the aberration of rays of large obliquity, while *coma* refers to the error of rays of obliquity of perhaps 1° or less.

brought together at the point F at a different distance from the lens than E. The resultant two image lines represent the sharpest image of an extra-axial point. As the inclination of the rays to the axis approaches zero, they draw together and fuse in the axial image. Since a line is an array of points, it follows that the best image of a vertical line perpendicular to the optic axis will be the overlapping vertical image lines of its points, while a horizontal line will be best imaged by the horizontal image lines.

Such an image of a line will not, in general, lie in a plane perpendicular to the axis, but rather in a curved surface. For a converging lens which is imaging distant objects, horizontal lines will be imaged in a surface concave toward the lens, and this surface will be closer to the lens than is the concave curved surface in which the vertical lines are imaged.
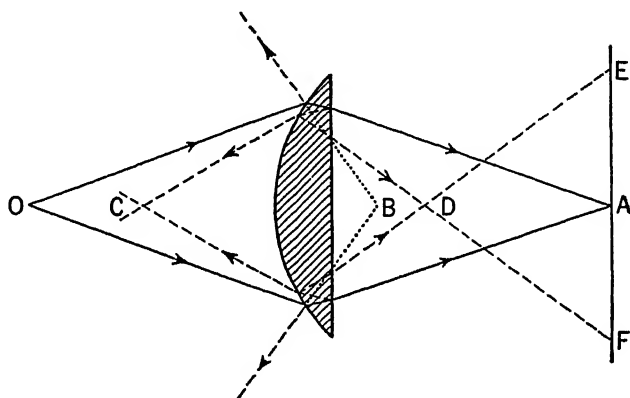
Fig. 27.   **Reflections at the Surfaces of a Plano-Convex Lens.**   The formation of flare is shown.

There exists, then, what is called an astigmatic *curvature of the image*. Furthermore, the removal of astigmatism from an image, by bringing the horizontal and vertical image-line surfaces together, will, in general, still leave such a curvature of the image, which must be independently corrected for in the lens design.

In addition to correcting the camera lens for the aberrations discussed above, it is highly desirable that the lens curvatures be so chosen as to minimize *optical flare*. Optical flare results when light reflected from the lens surfaces, which act as weakly reflecting spherical mirrors, is brought to a focus in such a way as to throw stray light on the photographic plate. A simple example is shown in Fig. 27. A beam of light from O falling on the plano-convex lens is brought to a focus at A. Part of the light is reflected from the first surface and diverges as if from a virtual image at B. This light cannot reach the plate unless it is further reflected from the lens mounting or other surfaces. The same is true

of light which is reflected from the plane surface and which is brought
to a real image at C. However, a part of the light reflected from the
plane surface will suffer a second reflection at the curved surface, as
shown, and passing through a real image at D, will fall on the region EF
of the plate, where it will cause a general illumination or flare over this
region. Of course, only a small fraction of the original light incident
on the lens reaches the flare spot. It may, however, be very trouble-
some, especially in the case of line spectra, where the direct image at A
contains only the light of one spectral line, or wave length, while beams
of many wave lengths striking the lens at slightly different angles may
contribute to the flare EF. No lens can be free of reflections. However,
in carefully designed lenses, it is possible to diminish flare: by avoiding
deep lens curves, since the amount of light reflected increases with the
angle of incidence; by avoiding air spaces between lenses, since an air
space means two reflecting surfaces each of which will reflect much more
than a glass-glass interface; and by arranging for the real images formed
by the reflected light to appear in places where they can readily be
blocked by small screens.

The ideal spectrographic camera lens, it is clear, should be free of,
or corrected for, chromatic and spherical aberration, coma, astigmatism,
and curvature of field. Such a lens would also be an excellent photo-
graphic camera lens. It is, however, impossible in an actual lens to
remove completely all the defects mentioned, and the best working
compromise is not usually the same in the two cases.

Spherical aberration and coma are exceedingly troublesome in either
case and should certainly be minimized. Chromatic aberration, how-
ever, is not necessarily damaging in a spectrographic lens; for the beam
of each different color is brought to a focus at a different angle with the
optic axis, and if it is brought to a focus at a different distance from the
lens, the focal surface, while not at right angles to the axis, may still be
nearly plane, although inclined. On the other hand, an achromatic lens,
corrected for two colors, will show "secondary chromatic aberration"
(page 51), or variation of focal length, for other colors. Such a lens,
if used as a spectrograph camera lens, will usually give a focal curve
which is convex toward the prism[45] and which, although nearly per-
pendicular to the optic axis, may be more curved than that of a simple
lens. As pointed out above (page 77) for a converging lens, the astig-
matic focal surface for horizontal line images is usually concave toward
the lens. Thus the astigmatism of the lens may be made to counteract
the chromatic curvature of the field. In fact, it is possible to introduce
for this purpose additional astigmatism from the prism by defocusing
the collimator lens slightly so as to send a converging beam through the
prism (page 55).

[45] H. Fassbender and A. Wetthauer, *Zeits. f. Instrukde.*, **33**, 265, 1913.

The variation of focal length caused by the astigmatism and field curvature of a lens depends on the angle to the optic axis at which the beam passes through the lens, while this angle differs for each wave length and is, in turn, fixed by the dispersion and setting of the prism. Thus, a camera lens may give a satisfactorily flat focal curve for one prism while, for a different prism or a train of two or more prisms, the curve may be quite different and unusable. Interesting examples of such cases are given by Plaskett[46] in his studies on the optical parts of the Victoria spectrograph.

When too great speed is not required, that is, for ratios of focal length to diameter of the order of f/20, single plano-convex or meniscus camera and collimator lenses of the same material as the prism may be used. Single lenses are especially common in the case of single-prism quartz spectrographs because of the problem, already pointed out, of a satisfactory material to combine with quartz in compound lenses. Large glass spectrographs with single lenses are, however, frequently seen. Single lenses are usually ground aspherical to remove spherical aberration, and the curvatures are chosen to reduce coma as much as possible. In instruments with one 60° prism and with simple lenses of the same material, the focal plane is nearly flat and is inclined at an angle of only about 25° to the optic axis. If two prisms are used, the field is generally more curved, though less inclined. The characteristics of single-lens instruments have been discussed by Hartmann[47] and by Eagle.[48]

For somewhat higher speed, say f/10 or f/12, camera lenses consisting of two separated lenses of the same material are frequently used in both glass and quartz optics. The extra surfaces give a better control of spherical aberration and coma, and a stop placed between the two lenses aids in reducing astigmatism. Such designs have been discussed by Hartmann[49] and Eagle.[50] Plaskett[51] gives the results of tests of several such two-component glass camera lenses in one- and three-prism spectrographs. These one-material lenses are, of course, not achromatic, and when they are used the photographic plate must be tilted.

The tilt of the photographic plate which results from the use of nonachromatic camera lenses gives a larger spectral dispersion than would result from the use of an achromatic lens with the same dispersing system. The ratio of the lengths of the spectrum without and with chromatic correction is the cosecant of the angle between the plate and the

[46] J. S. Plaskett, *Astrophys. J.*, **59**, 65, 1924.
[47] J. Hartmann, *Zeits. f. Instrkde.*, **20**, 19, 1900.
[48] W. H. Eagle, *Proc. Optical Convention, 1912*, II, p. 120.
[49] J. Hartmann, *Zeits. f. Instrkde.*, **24**, 257, 1904.
[50] W. H. Eagle, *op. cit.*
[51] J. S. Plaskett, *Astrophys. J.*, **29**, 290, 1904.

optic axis, and for a tilt of 25°, as found in simple lens systems, is about 2.3. There is, of course, no corresponding gain in resolving power, since each line image is wider in the same ratio. As was pointed out in the discussion of resolving power (Sec. 17), a gain in dispersion, even without an accompanying gain in resolution, may sometimes be advantageous. It should also be noted (see page 34, footnote) that the illumination in the case of a tilted plate of tilt angle θ is diminished by the factor sin θ.

Spectrograph camera lenses of speed higher than about f/6 are usually at least partially corrected chromatically. A notable exception, however, is the single lens of aperture f/1 made by Hilger for the night sky spectrograph of Professor McLennan at the University of Toronto.[52] This lens was ground aspherical to correct spherical aberration and was intended to be used only in the immediate neighborhood of the green auroral line. The great advantage of such a single lens is the much smaller loss of light by reflection from its two surfaces as compared with that from the six or more surfaces in a fast achromatic lens.

Numerous compound camera lenses have been described for high-speed spectrographs. Only a few will be mentioned. For use in the extreme ultraviolet, the quartz-water achromat designed by van Heel has already been mentioned. This camera lens has an aperture of about f/2.3; it is slightly undercorrected chromatically; the residual spherical aberration is reduced by aspherical retouching; and a flat field is obtained on a slightly tilted plate over a wide range in the ultraviolet. Examples of high-speed glass compound lenses will be found in the catalogs of such spectrograph manufacturers as Adam Hilger, Kipp and Zonen, and others.

A striking increase in the maximum aperture of spectrographic camera objectives has resulted from the observation of W. B. Rayton[53] that the problem of the design of such high-speed lenses is similar to that of microscopic objectives. Rayton was able, by enlarging and modifying the design of a 4-mm. microscope objective, to produce a successful f/0.6 objective of 32-mm. focal length. Higher apertures in microscope objectives require oil immersion, that is, an oil of suitable index of refraction between the objective and the object under examination. By application of this principle to spectrograph lenses, R. J. Bracey[54] developed, from a 2-mm. oil-immersion microscope objective, an f/0.39 spectrograph objective. The rear surface of the lens is almost in contact with the photographic plate, and a suitable immersion fluid is used between lens and plate. These high-speed lenses are designed for the study of the spectra of faint nebulae, and are to be used with the

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[52] J. C. McLennan and H. J. C. Ireton, *Proc. Roy. Soc.*, **129A**, 31, 1930.

[53] W. B. Rayton, *Astrophys. J.*, **72**, 59, 1930.

[54] R. J. Bracey, *Astrophys. J.*, **83**, 179, 1936.

spectrograph on the 200-inch telescope of the Mt. Palomar, California, Observatory. Each gives a flat, well-corrected field over a spectral range from 3600A to 5000A, and each represents nearly the attainable limits in aperture for its type of lens. In fact, the maximum attainable aperture for an immersion-type objective is set by the refractive index of the photographic emulsion, and the f/0.39 lens fails by only 10 per cent to reach this theoretical limit.

37. Resolving Power of Camera Lenses

It is of interest to note that, for any spectrograph, the factors which limit the definition of spectral lines at the two ends of the wave-length range may be different. At long wave lengths, definition may be limited by the width of the diffraction pattern. As has been pointed out (Sec. 17), the width of the first maximum of a diffraction pattern is $2f\lambda/b$, and thus is proportional to the wave length. Since, with a prism instrument, the dispersion decreases toward the longer wave lengths, this effect of wider lines at longer wave lengths often sets a limit both to definition and to resolving power at the red end of the spectrum.

On the other hand, residual lens aberrations which, regardless of wave length, are of nearly constant magnitude in the images, become increasingly important at shorter wave lengths. Lord Rayleigh has given as a criterion that the residual aberrations should have a magnitude of less than $\lambda/4$;[55] thus a lens perfectly satisfactory at one wave length may, at half that wave length, show a marked loss of definition.

Since, for most lenses, the residual aberrations are largely due to the outer zones of the lens, definition is often improved by stopping down the lens, and this improvement is most noticeable at short wave lengths. In a lens in which diffraction sets the limit, however, stopping down actually makes the definition worse at long wave lengths, since the width of the diffraction maximum is inversely proportional to the width of the diffracting aperture.[56]

38. The Use of Mirrors in Spectrographs

Mirrors may be substituted for collimator and camera lenses in spectrographs—in some cases, with marked advantage. In the extreme infrared, for example, the use of mirrors is made necessary by the lack of transparent optical material. In the visible and ultraviolet regions, mirrors are usually cheaper than lenses, especially in the larger diameters.

Chromatic aberration is, of course, absent in a mirror, since all wave lengths are reflected alike. In a concave mirror which has to render parallel the rays from a small source or to bring to a focus a parallel

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[55] J. W. Lord Rayleigh, *Scientific Papers*, III, p. 100.
[56] Cf., for example, *Zeiss Bulletin, Mess. 687*, on the quartz spectrograph Qu 24.

beam, spherical aberration may be avoided by the use of a paraboloidal mirror. However, the incident and reflected beams must make a certain angle with one another; and spherical aberration, since it is absent only for rays which pass through the focal point on the axis, will be present if the ordinary symmetrical center section of a paraboloidal mirror is used (Fig. 28a). The spherical aberration may be avoided by the use of the more expensive non-central (off-axis) section of the mirror (Fig. 28b).

(a) (b)
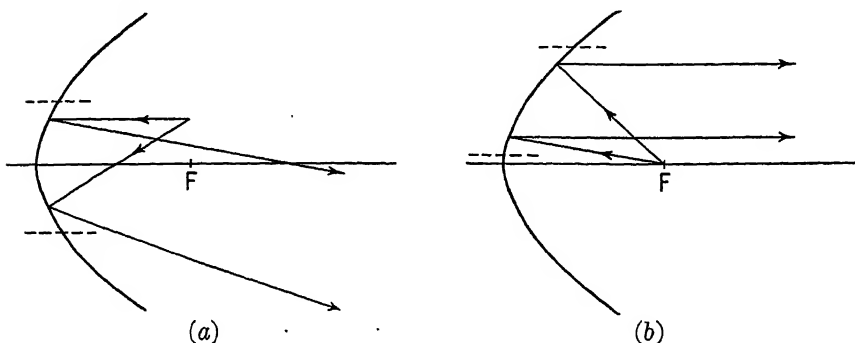
Fig. 28. (a) Spherical Aberration Produced by a Central Section of a Paraboloidal Mirror in Rays from an Off-Axis Point. (b) Aberration Avoided by Use of a Non-Central Section of Paraboloidal Mirror.

(a) (b)
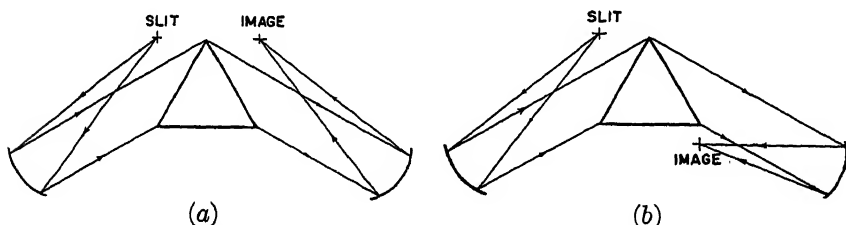
Fig. 29. Two Choices of Location of Image in a Mirror Spectrometer. Arrangement (b) leads to smaller aberrations than arrangement (a).

In the images of those rays that make a considerable angle with the axis of the paraboloidal mirror, coma and astigmatism will be found, and they cannot be corrected by any changes of the mirror figure; moreover, the field of the mirror, if used as a camera lens, is strongly curved. For these reasons, mirrors are not often used for photographic spectroscopy but are more often used as objectives in instruments of the monochromator type. In such instruments, one wave length, or a narrow wavelength region, is examined or utilized at a time, being brought to the exit point on the axis of the instrument by rotation of the dispersing prism or grating (see, for example, Fig. 99). It has been pointed out by Czerny and Turner[57] that some of the extra-axial aberrations are made worse

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[57] M. Czerny and A. F. Turner, *Zeits. f. Physik.*, 61, 792, 1930.

by the second mirror, if this mirror forms its image on the same side of the axis as the slit (Fig. 29a); on the other hand, the unsymmetrical form of instrument (Fig. 29b) permits the second reflection to cancel some of the aberrations introduced by the first and leads to a better image.

For large-aperture mirrors, the angle between the incident and reflected beams becomes undesirably large, with correspondingly large astigmatism. A device due to Pfund[58] avoids this difficulty by the addition of another reflection at a plane mirror. The plane mirror, P,
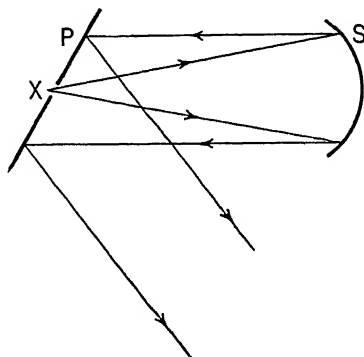
Fig. 30. Pfund's Use of a Plane Mirror to Avoid Astigmatism in the Use of a Paraboloidal Mirror.

pierced with a hole, is placed just behind the slit (Fig. 30). The light, rendered parallel by the paraboloidal mirror S is reflected back along the axis, hence without astigmatism, and is reflected off at any desired angle by the plane mirror. After dispersion, a similar system can bring the beam again to a focus. Spectrographs on this plan have been successfully built with apertures of f/2 or more.

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[58] A. H. Pfund, *J. Opt. Soc. Am.*, **14**, 337, 1927.

CHAPTER 5

Prism Spectroscopes and Spectrographs: Types and Use

39. Types of Prism Instruments

The simplest prism spectroscopes are the direct-vision instruments for hand use. They are only 4 or 5 inches long and consist merely of a slit which may be fixed or adjustable, a short-focus collimating lens, and a three- or five-piece Amici prism. There is no telescope or camera lens; the eye placed close to the prism acts as a camera lens and images the spectrum on the retina. A wave-length scale is sometimes projected into the field of view by a side tube and reflecting prism. This type of instrument is useful for examining arcs and
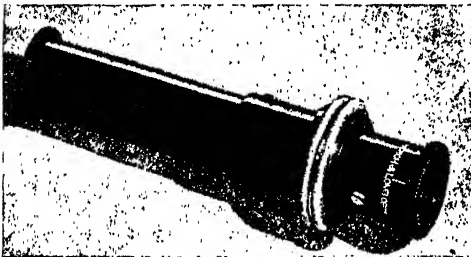
Courtesy of the Bausch and Lomb Optical Company.

Fig. 31. Direct-Vision Hand Spectroscope.

gas discharges for purity and approximate composition, or for observing the transmission of filters. A direct-vision spectroscope made by the Bausch and Lomb Optical Company is shown in Fig. 31.

More powerful direct-vision instruments with both collimator and telescope are occasionally seen, but more common are the fixed-arm combination monochromator and visual spectrometers, which often utilize a Pellin-Broca prism. An example is shown in Fig. 32. In this instrument, made by the Gaertner Scientific Corporation of Chicago, the collimator and telescope have a fixed deviation of 90°. The prism table and prism are rotated by a micrometer screw so that any desired wave length can be brought to the center of the eyepiece field. The micrometer screw also drives the flat spiral scale from which is read the wave length under the eyepiece cross hair. The spiral scale for the range 3950A to 8200A is 170 cm long in the regular model with prism of index $N_D = 1.65$, and 250 cm in the model with prism of index $N_D = 1.74$. By using the inner turns of the spiral for the violet end of the spectrum, and the outer turns for the less dispersed red end, the scale can be gradu-

ated in ten-angstrom intervals of approximately equal length throughout the range, and single angstroms can be estimated. By replacing the eyepiece with an exit slit, this instrument can be used as a monochromator or monochromatic illuminator for radiating a thermopile, photoelectric cell, or interferometer with light of a chosen narrow wave-length band. Similar wave-length spectrometers, but with a wave-length scale on a helical drum instead of on a spiral, are made by various manufacturers.
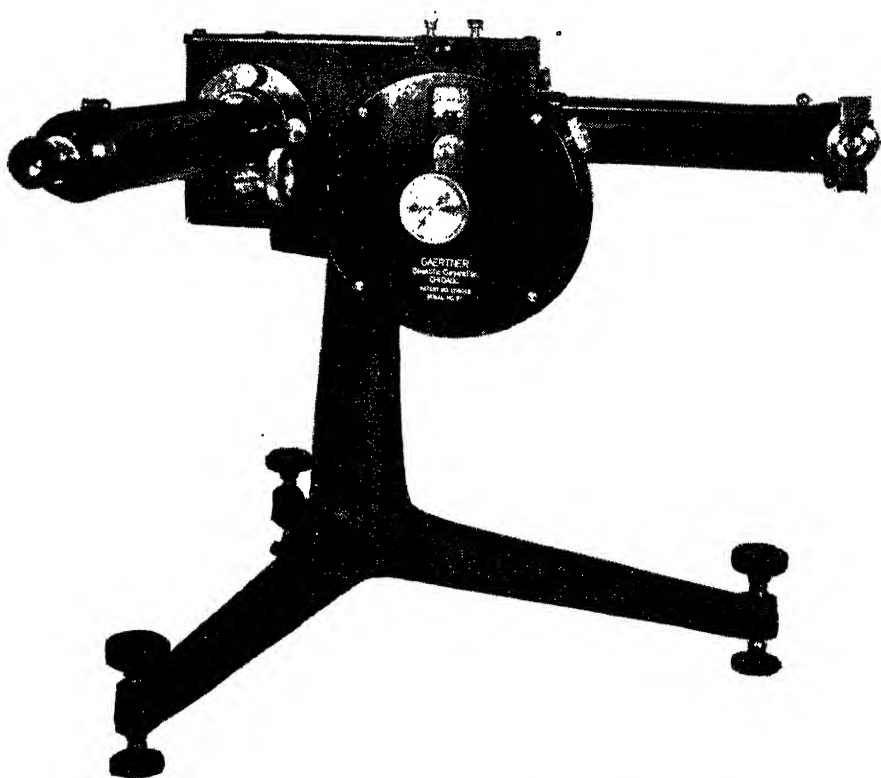
Courtesy of the Gaertner Scientific Corporation.

Fig. 32. Wave-Length Spectrometer or Monochromatic Illuminator with Constant Deviation of 90°.

For photographic work requiring only moderate dispersion, the telescopes can be replaced, in some instances, by a camera attachment.

An interesting example of a simplified constant-deviation spectroscope designed for a particular use is the Steelscope of Adam Hilger, Ltd. This instrument, shown in Fig. 33, has a condensing lens permanently mounted before the slit. Two glass prisms give sufficient dispersion for observation of the iron spectrum. The spectrum is viewed through a screw-focusing sliding eyepiece mounted on the telescope arm. An index on the sliding eyepiece marks the location of the prominent lines of eleven

elements commonly found in steel. When a steel sample is used as an electrode in an arc before the slit, an observer, having set the eyepiece at the position of any one of the eleven elements, can immediately detect the presence of the element and, by comparison with samples of known analysis, estimate the percentage. The instrument is largely used for the rapid sorting of steel scrap. A similar instrument is also available for the examination of brass and bronze for tin, lead, iron, and manganese.

Various other types of monochromators are seen, some arranged with two successive trains of optics to give greater purity of spectrum through

Courtesy of Adam Hilger, Ltd.
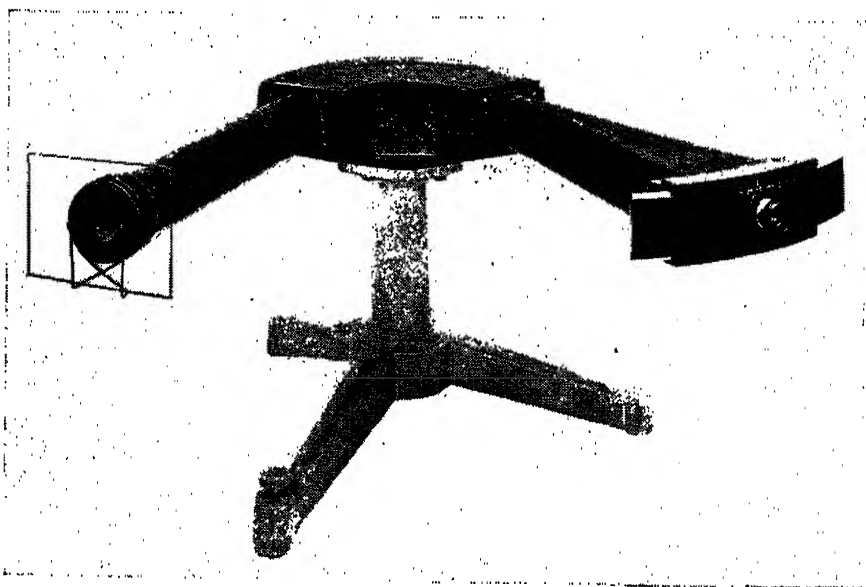
Fig. 33. The Steelscope, a Constant-Deviation Spectroscope for the Rapid Sorting of Steel Samples.

the elimination of stray light, and some arranged with more prisms to give greater dispersion. An example combining high dispersion with high purity of spectrum is the Müller type of instrument, made by Adam Hilger, Ltd. A schematic drawing of the arrangement is shown in Fig. 34. The light entering the slit S_1 is totally reflected at the prism U_1, and is collimated by the aspherical lens surface L_1, which is ground on the face of half-prism P_1. After reflection at the rear face of the second half-prism P_2, the light retraverses P_1 and L_1, and, after total reflection at the prism U_2, is focused on the slit S_2, whence it passes through the identical second half of the optical system. The resultant spectrum is much freer from stray light than one produced by a single monochromator, but the reflection losses are somewhat larger. The helical wave-length drum

D drives the micrometer screw *K*, rotating the table carrying the reflecting half-prism by means of the arm and sector shown. The instrument is provided with interchangeable optics of quartz, glass, rock salt, and
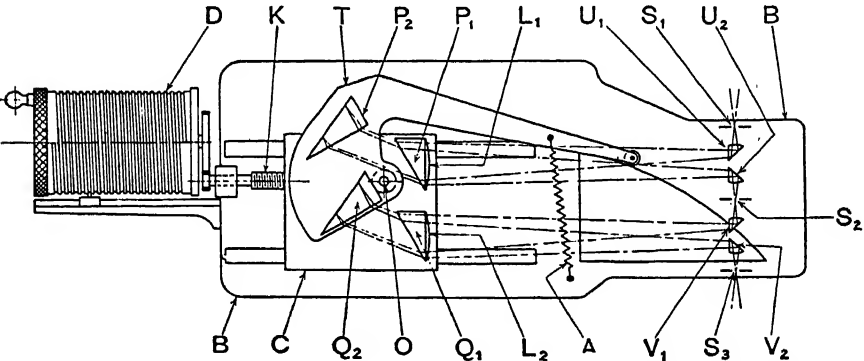
Courtesy of Adam Hilger, Ltd.

Fig. 34. The Müller Monochromator, for High Dispersion with High Purity of Spectrum.

sylvine, each with accompanying wave-length drum, and is thus usable with the following ranges of wave length and of dispersion:

Material	Calibration Range	Range of Dispersion (mm per angstrom)
Quartz.....	0.185 to 4.0μ	0.113 to 0.0038
Rock salt	.24 " 17.0μ	.098 " .0017
Sylvine....	.21 " 22.5μ	.21 " .0012
Glass....	.36 " 2.0μ	.033 " .00048

The instrument has an aperture of f/5; the scattered light with the quartz system is said to be less than $2 \cdot 10^{-5}$ of the monochromatic light; and the energy output, because of the large aperture and relatively small number of reflecting surfaces, is greater than that of any other double monochromator now on the market. Descriptions of numerous other types of single and double monochromators will be found in the periodical literature and in the catalogs of optical manufacturers.

It is impossible to describe all the variations of prism spectrographs which have been used to photograph the spectrum. A few examples will be given to illustrate some of the features and characteristics of such instruments.

The most common type of spectrograph is, doubtless, the Babinet-Bunsen, or one-way, instrument, in which the telescope has been replaced by a camera lens and plate holder. Because of the awkward length

introduced, this type is seldom made with lenses of focal length greater than one meter; shorter focal lengths are more usual. Although one-prism designs are typical, instruments with two or more prisms are seen where high dispersion combined with high light intensity is desired.

An example of a one-prism quartz spectrograph by Adam Hilger, Ltd., is shown in Fig. 35. The collimator and camera lens have equal focal lengths, about 60 cm for the D lines; the spectrum from 2000A to 10,000A is 221 mm long and is recorded on a single plate. The camera lens is designed to give an almost flat spectrum, so that thin plates are not required. The maximum aperture is about f/12. The instrument has a fixed adjustment of prism and lenses. Small corrections of focus to allow for temperature or other changes are made by small displace-
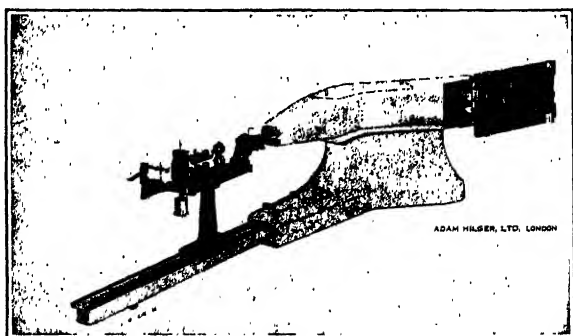
Courtesy of Adam Hilger, Ltd.

Fig. 35. One-Prism Quartz Spectrograph of "Medium" Size. This instrument is provided with an optical bench to hold an arc stand, condensing lens, or other accessories. Shown with arc holder and photometer for study of absorption of liquids.

ments of the slit. The slit is unilateral, with micrometer adjustment. Good features of this instrument, apart from optical excellence, are rigid all-metal construction, a device for printing a wave-length scale on each plate, and a removable optical bench for mounting the illuminating system before the slit. Spectrographs of this size are adaptable to many kinds of work where extreme speed or high dispersion are not required.

An interesting instrument of somewhat higher dispersion and much larger aperture is shown diagrammatically in Fig. 36. This instrument, which has been mentioned previously (page 52), was designed by A. C. S. van Heel and built by Kipp and Zonen, of Delft, Holland. As is usual in more rapid instruments (Sec. 25), the collimator lens has a much longer focal length than the camera lens—1000 mm and 160 mm, respectively, in this case. The lenses are quartz-water achromats, and the dispersing system is made up of three water prisms enclosed in quartz plates, with refracting angles of 36°, 72°, and 36°. The lenses are partially achro-

matized so that the plate tilt is small. The aperture of the camera lens is f/2.3. This instrument is intended especially for use in the extreme ultraviolet region, where, as previously noted, the dispersion of water is as great as, or greater than, that of quartz and the transparency better.

Glass spectrographs with camera lenses of large aperture are offered by most spectrograph manufacturers. The most interesting feature is the camera lens. High-speed camera lenses for spectrographs have already been discussed (page 80), with references to their description in the literature, and they will not be further described here. These instruments usually sacrifice dispersion to speed, and are intended for the examination of faint sources, as in Raman, fluorescence, or nebular
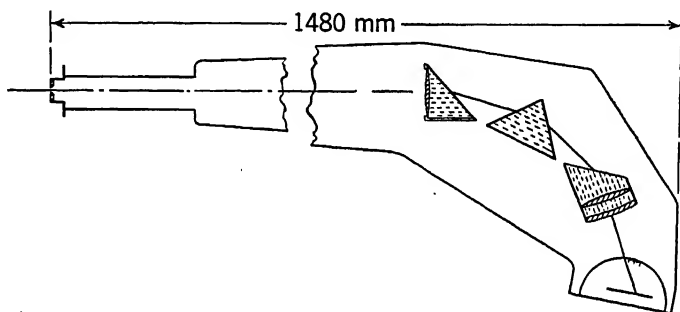
Fig. 36. Diagram of Large-Aperture, Two-Prism Spectrograph with Quartz-Water Achromatic Lenses and Water Prisms.

spectroscopy, or for the examination of sources of very short duration or rapid variation.

An example of a high-aperture glass spectrograph is the Raman spectrograph of the Gaertner Scientific Corporation, shown in Fig. 37. This instrument has two dense flint-glass prisms of 60° angle. The camera lens has a focal length of about 300 mm and an aperture ratio of f/3.5. The spectrum from 4046A to 6234A is 39 mm long.

Where more dispersion is desired than can be attained in one- or two-prism instruments of the Babinet-Bunsen type, within the limit on the focal length of the lenses set by reasonable size, two possibilities present themselves. These are the multiplication of the number of prisms, and the use of longer-focus lenses in the Littrow type. Multiple-prism instruments offer the advantage of high dispersion with high resolving power, because of the increase in length of the prism base. At the same time, the illumination can be high, since the light loss does not increase proportionately with additional prisms, and, furthermore, lenses of relatively large aperture can be used, since the dispersion is gained by large $d\theta/d\lambda$ rather than by large f in the relation $dx/d\lambda =$

$f(d\theta/d\lambda)$.   The cost of good-sized prisms makes these instruments rather expensive.   If stigmatic spectra are needed, or if higher illumination is needed for studies of relatively faint spectra, they may, however, be preferred to grating instruments of equivalent resolving power.   A multiple-prism instrument, with variable angle for the camera to accommodate any number of prisms up to six, has been described by J. S. Foster.[1]   The collimator and camera lenses are doublets with 115-cm focal length and 7.6-cm aperture; the prisms have circular faces 6 cm in diameter.   It will be seen that the prisms do not utilize the full aperture of the lenses, especially in the horizontal direction.   The dispersion with six prisms is 2A/mm in the violet.   Numerous arrangements for multiple-prism trains are described in Kayser, Volume I, Chapter V.   Because of the small demand for such specialized instru-

Courtesy of the Gaertner Scientific Corporation.

Fig. 37.   Two-Prism Glass Spectrograph of Aperture F/3.5.

ments, multiple-prism spectrographs are not regularly offered by the manufacturers.   Three-prism spectrographs, with a choice of several camera focal lengths, are built by C. A. Steinheil-Söhne of Munich and by Carl Zeiss, of Jena.   The Zeiss instrument has a modified Pellin-Broca prism between two 60° prisms, and a coupling which rotates all three prisms so as to give a constant deviation of 90° for the ray at minimum deviation.[2]   If a mirror is placed after the third prism, this system is also usable with an autocollimation camera of 130-cm focal length.   The dispersion, 2A/mm at 4000A, is that of six prisms, while the resolving power is that of 420 mm of prism base.

Where good dispersion with moderate illumination is desired, Littrow spectrographs are an almost universal choice and are offered by nearly all makers of spectrographic equipment.   The principle of the Littrow, or autocollimation, type has been mentioned previously.   A reflecting surface behind the prism system returns the light through this system

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[1] J. S. Foster, *J. Opt. Soc. Am.*, **8**, 373, 1924.

[2] Designed by K. Försterling.   Description in *Handbuch d. Physik*, V. 18, p. 330

and through the lens, which serves both as collimator and camera lens. The arrangement is economical, since the lens and prism requirements are exactly half those of the conventional type; and, since its size is approximately half that of the other type, it is conveniently compact. Reflected and scattered light are, however, somewhat more troublesome than in the one-way type.

A Littrow instrument, manufactured by the Bausch and Lomb Optical Company of Rochester, N. Y., is shown in Fig. 38. Interchangeable optical systems are provided, with the lens and 30° half-prism of quartz, or of glass of refractive index 1.625. The lens has a focal length of 1827 mm at 5893A, and a diameter of 70 mm. The prism has a height of
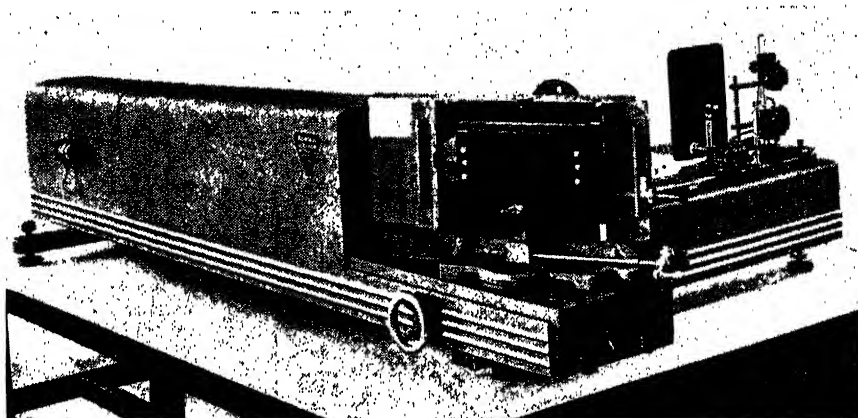
Courtesy of the Bausch and Lomb Optical Company.

Fig. 38. Large Quartz Spectrograph of Littrow Type. Front view showing plate holder. A rigid side arm at the rear holds an arc holder and condensing lens before the slit.

57 mm and a refracting face of 95 mm, so that the lens aperture is almost completely utilized.

The instrument base is a hot-rolled steel U-beam of extreme rigidity; the plate holder is carried on a large casting mounted on a large turret-bearing centered directly below the middle of the plate. This construction gives extreme stability, along with the desirable rotation of the plate about an axis through the plate surface. The resultant weight (630 pounds) is an advantage for many uses because of the freedom from disturbance by jars and vibrations.

The entire spectrum produced by the glass optics, 3550A to 10,000A, covers two ten-inch plates; the spectrum produced by the quartz optics, 2100A to 8000A, covers three such plates. To change from one region to another requires rotation of the prism, translation of the prism and lens to a new focus, and a change of plate tilt. All these adjustments are made from the plate-holder end of the instrument. A calibrated microm-

eter screw acting on a hardened steel arm on the plate-holder head rotates it against the restoring torque of a spring. The lens and prism are mounted on a carriage, which moves on two steel rails and is driven by means of a wire cable actuated by a hand wheel. A lens and mirror on the side of the spectrograph permit the carriage position to be read on a scale which is illuminated by a small electric lamp. The prism is rotated by an arm which is fastened to the prism table and which, as the table moves, presses on one or another of several micrometer screws.

λ	(A. U. per mm) Quartz	Glass
2180	1.54	--
2333	1.93	--
2860	3.64	--
3556	7.1	2.9
4365	13.6	6.3
4896	19.0	8.9
5593	26.7	13.8
6315	35.9	20.3
7298	50.1	29.8
8274	63.3	41.4
10267	85	63.8

Courtesy of the Bausch and Lomb Optical Company
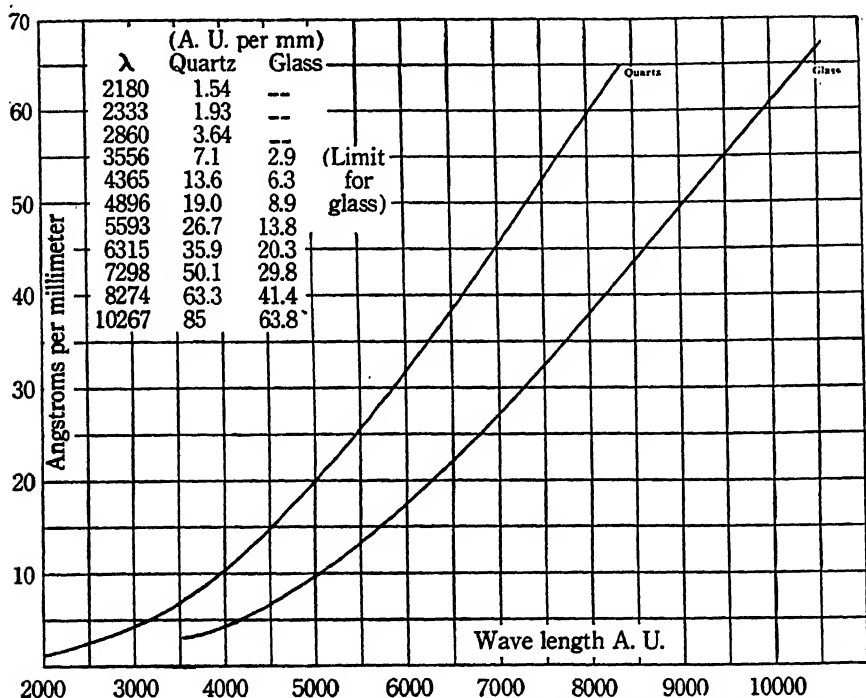
Fig. 39. The Reciprocal Linear Dispersion of the Bausch and Lomb Littrow-Type Spectrograph for Glass and for Quartz Optics.

These screws are accurately set to bring on the plate that portion of the spectrum which is in focus at the corresponding position of the carriage. Ten positions are provided for the quartz optics and seven for the glass, and so almost any desired region can be brought to the center of the plate. The slit is the bilateral one illustrated in Fig. 15. It is almost completely enclosed and is provided with a quartz plate or lens in front to exclude dust. Ways carry a Hartmann diaphragm close to the slit, and a shutter to control exposures is provided back of the slit.

The dispersion of this instrument for both glass and quartz optics is shown in Fig. 39. It is sufficient for the examination of any but the most complicated spectra and for the determination of wave lengths

in most regions to within a few hundredths of an angstrom unit. Spectrographs of these general characteristics are offered by several manufacturers and, second perhaps to single-prism quartz spectrographs, are the most popular instruments for general-purpose use in research and industrial laboratories.

Adam Hilger, Ltd., offers a universal autocollimation spectrograph in three sizes, with lenses of 100-, 150-, and 300-cm focal length, respectively. Five interchangeable optical systems are provided, namely: concave grating, 30° quartz prism and lens, 30° glass prism and lens, one 30° and one 60° glass prism and achromatic lens, plane grating and achromatic lens. This instrument is, of course, extremely versatile.
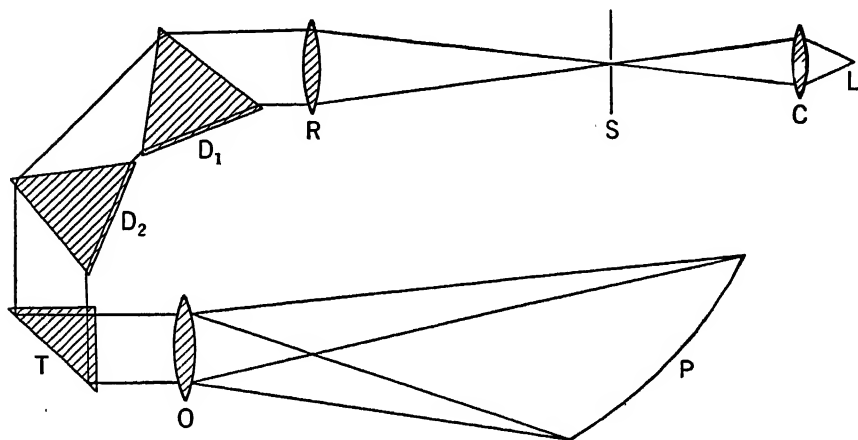
Fig. 40.   Diagram of Mannkopf Spectrograph with Two 60° Prisms and One 45° Totally Reflecting Prism to Give a Total Deviation of 180°.

In a laboratory where much work is to be done, it may be found more convenient, however, to have two or more independent instruments.

Mannkopf[3] has pointed out that in a spectrograph with both collimator and camera lenses, the addition of a 45° totally reflecting prism to a two- or three-prism train results in the compactness and rigidity of the autocollimation type and the freedom from reflections and scattered light of the one-way type as well. A diagram of a two-prism instrument is shown in Fig. 40. The light from the slit S, after collimation by the lens R and dispersion by the prisms D_1 and D_2, is bent through 90° without additional dispersion by total reflection at the prism T, and thus suffers a total deviation of approximately 180°. The return path through the lens O to the photographic plate is then nearly opposite to the collimator axis. With three prisms the two rays might cross, so that the plate holder would be above the slit. In either case, the instrument is nearly

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[3] R. Mannkopf, *Zeit. f. Physik*, **72**, 569, 1931.

as compact as the autocollimation type and can be mounted on a rigid girder. A front-surface glass mirror or a metal mirror can be substituted for the totally reflecting prism, and is, in fact, necessary in cases where a deviation by reflection of other than 90° is required. For this reason, single-prism quartz instruments have been built by the Gaertner Scientific Corporation, with one reflection at a mirror producing a change of about 150° in the direction of the beam, to make the total deviation 180° (Fig. 41). These instruments, in contrast to the autocollimation type, require an extra lens as well as the reflecting prism or mirror. The extra expense may be justified in cases where scattered light is objectionable, as in
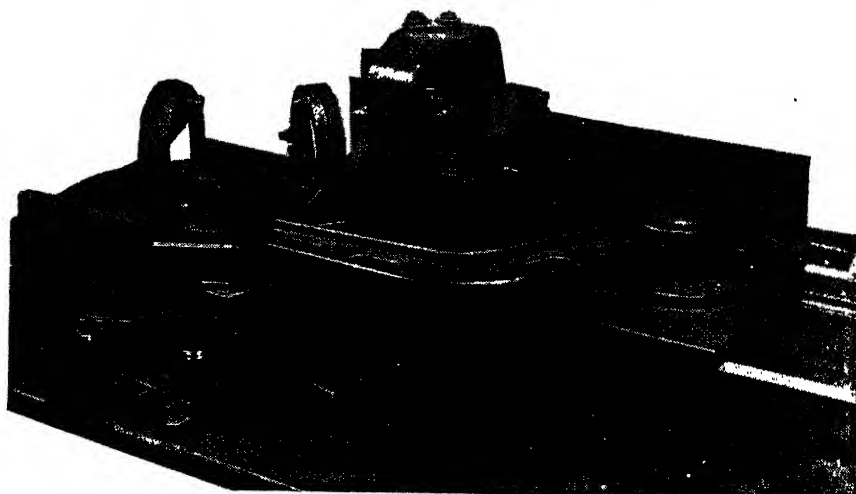
Courtesy of the Gaertner Scientific Corporation.

Fig. 41. Optical System of the Gaertner Large Quartz Spectrograph. The beam, after traversing the collimator lens, 60° prism, and camera lens, is reflected by the plane mirror to the plate.

quantitative or absorption spectroscopy. The elimination of scattered light is discussed in Sec. 44. It will be found, in general, that scattered light can be sufficiently reduced in the autocollimation type if a small portion of the center of the lens can be blocked off without too much loss of light or of optical field, or if the lens can be slightly tipped or twisted without too much loss of definition.

Although the spectrographs described include most of the types which are readily available and commonly used, an examination of the indices of periodical literature or of the larger reference works and makers' catalogs will reveal special instruments constructed to meet special demands or problems. Many factors must be considered in the choice of an instrument for a particular problem or for general laboratory use. Some of these are cost, availability, and space, as well as illumination, dispersion, range, and resolving power. A suitable instrument can

usually be selected by a process of elimination. In general, it may be said that in case of doubt it is well to err in the direction of too large dispersion and resolution rather than too small, since often the need for extreme precautions and much labor to attain sufficient accuracy in measurement and interpretation is thus avoided.

40. The Adjustment of Spectroscopic Instruments

It was pointed out on page 55 that the astigmatism is at a minimum and the definition of the spectra the best if

1. The prism is traversed by parallel light.
2. The slit is parallel to the prism edge.
3. The light rays are parallel to a principal section of the prism.
4. The rays pass through the prism at minimum deviation.

In the case of prism spectrometers intended for visual observation and for measurement of angles, arrangements are provided for focusing and leveling the collimator and telescope independently, for leveling and rotating the prism table, and for swinging the collimator or telescope, or both, about the axis of the prism table. The adjustment of the instrument to meet the above requirements can be carried out by a logical procedure which has often been described.[4] The description will not be repeated here, since this type of spectrometer is relatively little used except in the measurement of prism angles and of indices of refraction. In monochromators and in spectrographs for photographic use, most, or all, of the necessary adjustments are made, at least approximately, by the manufacturer. Some notes will be given, however, for aid in checking the settings or in adjusting new designs.

In order that the prism shall be traversed by parallel light, the slit must be placed at the exact focal plane of the collimator lens. If the collimator lens is achromatic and is to be adjusted for visible light, the setting is easily checked. If it is possible to look at the slit through the collimator lens, either directly or by the use of a plane mirror set at an angle before the lens, the slit may be illuminated from behind and viewed through the lens with a telescope. If the telescope has previously been focused on a very distant object, it is then only necessary to move the slit in or out until it is seen sharply through the telescope.

Another method of focusing the collimator is to mount a fine hair across the widely opened slit and to view this hair through a Gauss, or illuminating, eyepiece. If a good plane mirror is placed behind the collimator lens and the eyepiece illuminated with white or any desired monochromatic light, a reflected image of the cross hair should be seen

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[4] H. Kayser, *Handbuch d. Spectroscopie*, Vol. I, p. 335; G. S. Monk, *Light*, p. 426, New York: McGraw-Hill Book Co., 1937.

beside the cross hair. The collimator is adjusted for parallel rays when, on moving the eye slightly, no parallax is seen between the cross hair and its image.

If, as, for example, in quartz spectrographs, the collimator lens is not achromatic, it can of course be focused for parallel rays for only one wave length. The first method described cannot be used, but the adjustment with the Gauss eyepiece can be carried out if monochromatic light is used for illumination. Thus, with a sodium burner, the collimator can be adjusted for 5893A. If adjustment for some other wave length is desired, the lens–slit distance can be measured, the change in focal length for the new wave length can be computed by aid of the tables for the index of refraction of quartz, and the necessary change can be made. In the case of quartz spectrographs, some spectroscopists focus the collimator for a wave length in the middle of the instrument's range. Eagle,[5] however, finds that focusing for the shortest wave length in the range gives much better definition at that end, while the definition is still good enough at long wave lengths, where the smaller dispersion makes the requirements less critical. Furthermore, the spectrum is longer, the plate tilt is less, and the required radius of curvature of the plate is greater than it is when the collimator is focused for a longer wave length.

Lippman[6] has described an excellent method of focusing the collimator lens. Two thick plane-parallel glass or quartz plates placed on one another at right angles are set between the collimator lens and prism so as to make equal angles with the light beam. A pair of Michelson interferometer plates of glass or quartz can conveniently be used. Since a plane-parallel plate set obliquely will displace the image formed by any but a parallel beam passing through it, the upper and lower halves of the slit image, when seen through this apparatus, will appear relatively displaced unless the collimator is in focus. The lines from a source of line spectra, after passing through this arrangement and through the prism, may be examined at the focal plane of the camera lens with an eyepiece or photographically. This method, then, can be used in any region.

The conditions that the slit be parallel to the prism edge, and that the light rays be parallel to a principal section can usually be fulfilled sufficiently well by observation of the spectrum in the focal plane of the camera lens. It is best to use a many-lined spectrum, as of the iron arc, and to reduce the slit length to a millimeter or two. The spectrum can be observed visually, or better—and in the ultraviolet, necessarily—photographically. If the prism is level, the light rays are parallel to a principal section, and the spectrum must extend parallel to the plane of the prism base, which is also parallel to the spectrograph table. Also,

[5] W. H. Eagle, *Proc. Opt. Conv. London, 1912,* II, p. 120.
[6] G. Lippman, *Comp. Rend.,* **129,** 569, 1899.

if the slit is parallel to the prism edge, the spectral lines will cut the length of the spectrum at right angles. It must be remembered, however, that since the spectral lines are curved, adjustments must be made until the spectrum appears to be made up of vertical line segments arranged in a horizontal row across the plate.

The condition that the rays pass through the prism at minimum deviation can, of course, be satisfied for only one wave length in the range covered by a spectrogram. The wave length chosen is commonly the one in the geometrical mid point of the spectrum. This choice is unavoidable in multiple-prism instruments since otherwise the outer rays would traverse the final prisms too far from minimum deviation. It has been found, however, that in single-prism quartz instruments, the prism should be set at minimum deviation for a ray near the short wave-length end of the spectrum, 2100–2200A.[7] This setting gives somewhat less dispersion but less plate tilt and plate curvature than a setting at minimum deviation for a mean or long wave-length ray.

The prism setting to give minimum deviation for any chosen wave length can be calculated readily, since in this case $\sin i = n \sin (\alpha/2)$, and an approximate setting can then be made with the help of a protractor, or, if more precision is desirable, the angles can be measured with the help of a small spectrometer. Finally, the setting can be checked by observing the spectrum with a fixed eyepiece or photographically to see whether a small rotation of the prism shows the desired ray to be at minimum deviation. If a train of several prisms is to be adjusted, they can be set at minimum deviation one after the other, beginning with the one nearest the collimator, since the setting of each prism depends only on the angle at which the chosen ray comes to it from the preceding prism and is not influenced by the succeeding prisms.

The final adjustment is the determination of the distance of the photographic plate from the camera lens, and of the plate tilt. In fact, aside from the slit width and orientation, these settings are the only variables in many commercial instruments. They cannot be permanently fixed, since they are affected by temperature and pressure variations (see Sec. 45).

Many devices have been used to provide a variation of plate tilt. Whatever plan is used, the settings should be calibrated and definitely reproducible. It is a great advantage if the rotation of the plate is about an axis which lies in the plane of the plate at some point of the spectrum. Then this point can be brought into focus and the plate rotated about it to bring the whole plate into focus. Rotation about an axis in the plate is mechanically more difficult to arrange than about an axis at the end of the plate holder, and so is often not provided. It is worth insisting

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[7] Eagle, *loc. cit.*

on, however, if frequent readjustments of the instrument are to be required.

It is usually best to make the adjustment of the plate distance by moving the camera lens. The design of the plate holder can be simplified if this motion is separated from that of the plate tilt. In single-prism instruments, however, the final focusing adjustment is sometimes made by displacing the collimator lens or the slit. Each of these devices has the disadvantage of disturbing the collimation of the light striking the prism. The required movement can be relatively small, however, and the effect on the parallelism of the collimator beam need not be significant. Moreover, since temperature changes affect the focal length of the lenses, thermally induced errors of collimation may be partially compensated by the adjustment. In whatever way the focusing is done, the settings must be accurately reproducible and a good scale for reading the settings provided.

For the final focusing, a light source should be provided which emits numerous lines of good intensity well distributed through the spectrum. For instruments of medium to large dispersion, the iron arc is a simple and satisfactory source, with many fine lines throughout the visible and ultraviolet regions. Above 6000A, the iron lines are less numerous and less intense. A gaseous discharge tube containing neon or argon may be found convenient in this region. Discharge tubes with air or carbon dioxide have been recommended in the visible and ultraviolet because of the many fine lines in their band spectra. For spectrographs of small dispersion, the spark spectrum of titanium has been used. The titanium lines, while not so numerous as those of iron, are rather uniformly distributed throughout the whole photographic region.

After a suitable light source has been chosen, it is necessary to locate the source on the optic axis of the collimator. The source is first placed at a distance from the slit which is determined by the condensing lens and the type of illumination to be used (see Sec. 19). The alignment may be carried out by any of several methods, and must be done before the condensing lens is put in place.

The simplest procedure, perhaps, is that of visual observations at the plate end of the spectrograph. If the slit is opened to a width of a millimeter or two, an eye placed a foot or more back of the focal plane and looking toward the camera lens will see through each wide spectral line an image of the light source in the corresponding color. The light source should be moved until this image appears to be exactly in the middle of the objective when the eye is on the central line of the exit slot; it will then be in proper alignment. It is possible, and sometimes desirable, to locate the line of the collimator axis before the source is placed in position. If the region before the slit is strongly illuminated, objects there can be recognized by an observer looking through the

spectrograph, and a marker can be put in the center of the field to indicate the proper position for the light source.

A second and inverse procedure is to place a small light, such as a flashlight bulb, on the central line of the exit slot in the regions where the visible spectrum falls. The lamp then sends light back through the spectrograph, and a bundle of light will emerge from the slit, which can easily be seen if the observer looks toward the slit or can be caught on a card to fix the line of the axis.

Both of these methods are usable only where some part of the visible spectrum falls on the plate holder. If a spectrograph must be lined up for use in the invisible ultraviolet or infrared regions, it is probably simplest to place a small flashlight bulb a few feet in front of the wide-open slit. The small light bundle which passes through the slit can readily be seen on the collimator lens or on a card placed close before or behind this lens. The alignment can be adjusted until this beam is in the center of the lens; the bulb is then on the axis. The light source itself may, of course, be used if convenient, provided its luminous region is small enough in extent.

After the proper location for the light source has been determined, the condensing lens, if one is to be used, can be introduced. If it is to image the light source on the slit, the optics should then be filled with light. An eye placed at or near the focal plane should see the prism completely and uniformly illuminated with whatever color is brought to a focus at that point. If, on the other hand, the condensing lens is placed just before the slit and images the light source on the optics, an eye similarly placed will see the prism filled with light only if the source image fills the optics, and will see it uniformly illuminated only if the source radiates uniformly over its entire area.

With the light source and condensing lens in place, focusing of the spectrograph can be undertaken. If the approximate setting of tilt and focus is not known, it is expedient first to reach an approximate setting by viewing the spectrum on a screen placed in the plate holder. In the visible spectrum this screen can be a piece of ground glass or an old photographic plate which has been lightly fogged and processed. In the ultraviolet a fluorescent screen must be used, which may be a piece of uranium glass or a photographic plate which has been fixed without development and coated with a fluorescent solution. If the slit is opened one-tenth or two-tenths of a millimeter, the spectra can easily be observed with an eyepiece if the observer looks toward the prism. A few lines ruled or scratched on the screen will make it easier to tell when the spectra are in focus on the screen. With a little practice, both the tilt and focus can be adjusted with considerable accuracy.

The final setting must be made photographically. The slit is closed to the optimum width (see page 106) and a test plate taken to fix the

best exposure time. For this purpose a series of exposures with the time increasing by multiples of about 3—as 0.3, 1, 3, 10, 30 seconds—will make it possible for the best time to be chosen. A series of spectrograms can then be made on a plate, corresponding to progressive changes of focus. The size of step in these changes will depend on the aperture of the camera lens, which fixes the rate at which the beam diverges on either side of the focus. In Fig. 42, $F/D = dx/dl$: $dx = F/D \, dl$. But F/D is the f/-number of the lens, or $dx = $ (f/-number)dl.
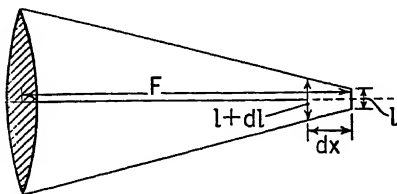
Fig. 42.   The Effect of Lens Aperture on Sharpness of Focus.

The change in lens setting to make a perceptible change in line width is then proportional to the f/-number. The least perceptible change in line width depends chiefly on the plate grain, if the plate is viewed with a magnifier of sufficient power, and is generally of the order of one-tenth to one-twentieth of a millimeter. Thus, for many common spectrographs, where the f/-number is 10 to 20, dx will be from one-half to two millimeters.

If the initial approximate setting has been successfully carried out, a plate with eight or ten equally spaced displacements of the focusing adjustment should show the spectral lines passing through the best focus. If the tilt or curvature of the plate is not correct, only a small region of the plate will be in the best focus at any setting, and on successive spectra the region of best focus will move systematically along the spectrum. A rough calculation from the known constants of the spectrograph will indicate the proper adjustments; one or two more test plates should suffice to bring the whole plate into the best focus. It is essential that the tests carry the lines completely through the best focus so that the lines can be seen spreading on either side of the optimum settings; a conclusion that the sharpest lines have been attained is not safe if it is based upon observations on one side of the focus only. It will often be found in both prism and grating spectrographs that the lines do not broaden uniformly as they go out of focus, but rather break up into two or more lines. While not the ideal situation, this condition does not necessarily involve any defect of the lines at the best focus.

It is sometimes desirable to determine the exact focal curve of a complete spectrograph in more detail than described above. This curve depends, as mentioned earlier (page 79), not only on the camera objective, but also on the number, dispersion, and adjustment of the prisms, and on the correction and focusing of the collimator lens. A description of the procedure and examples of the results will be found in the paper by Plaskett[8] referred to previously.

[8] J. S. Plaskett, *Astrophys. J.*, **59**, 65, 1924.

There are two reasons for the careful alignment of the light source on the collimator axis and for the adjustment of the collimator to fill the optics with light. One reason is, of course, that the maximum illumination of the spectra is thus assured. The other reason is that if the spectrograph optics are not perfect, it may be found that the position of the line image depends on the position of the light source. If the full aperture of the optics is always utilized, errors in line position arising from this apparent displacement will be avoided.

41. The Testing of Spectroscopic Instruments

In the ideal case all light rays of the same wave length passing through the spectrograph slit and striking the collimator lens should be brought to a focus in the diffraction pattern of the line. The obliquity of the rays or the distance from the slit of the light source, or of its image formed by the collimator lens, should have no effect on the line position. Unfortunately, such perfection of the optics cannot be assumed, even in expensive commercial instruments. If the position, sharpness, and form of the line images are of importance, as they are in practically all spectrographic researches, tests of the quality of the optics should be undertaken.

The simplest test is an examination of the character of the spectral lines formed by the instrument when spectra are made, as described above, in the course of adjusting the instrument with the help of a light source emitting fine spectral lines. The spectrograms at the best focus, when examined with an eyepiece, should show very sharp line images, without any fuzziness or faint companion lines on either side. It should be remembered that the apparent sharpness of the lines depends on their density and on the character of the photographic·plate. Heavily exposed lines tend to broaden out because of the turbidity of the plate. Then, too, with plates of high contrast, the presence of fuzzy edges or of faint companions is much less noticeable than with low-contrast plates. The faint imperfections may then be below the threshold sensitivity of the plate. It is always well to be suspicious of test plates submitted for a spectrograph if they have been made by light exposures on extremely high-contrast plates.

With some experience it is possible to judge whether or not the line sharpness is adequate. If it is not, additional tests are required to locate the seat of the trouble. Such tests may be desirable in any case, since too much confidence should not be put in subjective judgments.

The most complete tests are doubtless those made with an interferometer, such as the Twyman-Green or similar arrangements.[9] The

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[9] Cf. W. E. Williams, *Applications of Interferometry*, p. 65. London: Methuen, 1928, F. Twyman, *Phil. Mag.*, **42**, 777, 1921.

use of an interferometer permits individual tests of each lens and prism, and the exact location and quantitative evaluation of the imperfections. Some manufacturers, notably Adam Hilger, .Ltd., now use the interferometer in the final testing and retouching of all spectrograph optics. The procedure will not be described here in detail, since the equipment is not generally available.

A powerful and simple test of the complete spectrograph described by Hartmann[10] is readily carried out and does not require great experience in interpretation. It rests on the fact, noted above, that all rays of one wave length passing through the slit and optical system should be brought to a focus in the same sharp line image, while imperfections or aberrations in the optics may cause the beams traversing different parts of
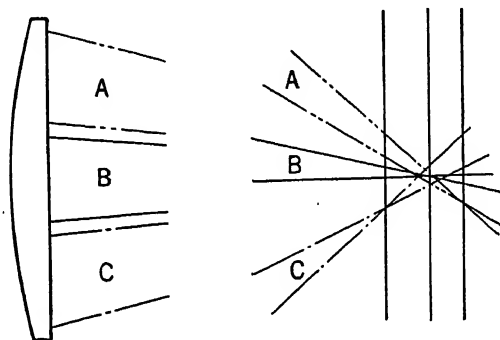
Fig. 43. The Hartmann Test of a Spectrograph. The beams, *A*, *B*, and *C* (left), emerging from camera lens are brought to focus, because of imperfections in the optical system, at different distances from the camera lens and at different points along the plate.

the system to come to a focus not only at different lens-plate distances, but also at different plate positions (Fig. 43). If every part of the optics contributes to each part of the line image, faulty optics will result in a fuzzy or irregular line; if beams from different regions of the optical system form different parts of the line, faulty optics will result in a crooked line. The test is arranged so that the line images formed by different parts of the optics are compared in position and sharpness.

The slit is opened to a width of about $10(f\lambda/d)$ (Sec. 42), so that the central maximum of the diffraction pattern of the slit is much narrower than the collimator lens. A small light source placed before the slit on the collimator axis sends light through a narrow central region of the optics; if the source is displaced by stages to either side, regions to the side of the center are illuminated in turn. Hartmann utilized a hydrogen discharge tube placed 25 cm before the slit. The hydrogen spectrum, however, is not suitable in the ultraviolet and, in any case, a source

[10] J. Hartmann, *Zeits. f. Instrkde.*, **20**, 47, 1900.

somewhat richer in lines is more convenient. At the University of Michigan, a condensed spark between iron electrodes, one-eighth inch in diameter with one-eighth-inch gap, has been found satisfactory. A lens before the slit to image this source on the optics somewhat shortens the exposure.

The light source is moved across the field so that successive sections of the optics are illuminated, and, with the aid of a Hartmann diaphragm, a series of adjacent spectra are recorded on a plate; it is desirable to include at least five positions. The spectra should be made at the setting of best focus. It may be difficult, however, to determine the setting exactly, especially if the optics are imperfect, and in that case two or three sets of test spectra should be made at settings near the apparent best focus. It is clear that in the ideal case the five beams from the five regions should come to a focus at the same setting, giving for each wave length five spectra in perfect alignment (Fig. 44a). A progressive displacement will be found before (44b) or behind (44c) the best focus.

Fig. 44. Position of Five Beams in Hartmann Test of a Good Optical System: a, at Focus; b, in Front of Focal Plane; c, Behind Focal Plane.

If, however, there are significant lens aberrations, or inhomogeneities in the prism or lens material, some of the beams will be diverted from their proper direction. There will be no plate position at which all five spectral lines will fall in a line, or at which the out-of-focus spectra will show the progressive displacements of Fig. 44b or 44c. Rather, at different settings two or more spectra will line up, while the others will be more or less displaced. Such results as are shown in Fig. 45a or 45b will be obtained. When the whole optics are illuminated at once, the spectral line receives contributions from all the sections and will have a total width corresponding to the different line positions. Accordingly, the amount of the displacement can be measured with a comparator, and if a tolerance is placed on permissible line width, a decision can be reached as to what sections of the optics must be diaphragmed off in order to attain the width.

Fig. 45. Position of Five Beams in Hartmann Test of a Defective Optical System for Two Different Focus Positions, a and b.

When the Hartmann test reveals defects in the optics, the question arises as to which component of the system is responsible. Although the lenses or, in the Littrow case, the totally reflecting prism may be responsible, suspicion falls first on the dispersing prism or prisms. The difficulty of obtaining sufficiently large homogeneous pieces of glass and, especially, of quartz leads sometimes to the use of second-quality material. If another prism is available, it can be substituted and the test repeated

to see whether the result is altered. If substitution is impossible or if suspicion falls on the lens system, a test can be made without the prism. In the Littrow type, a front-surface plane mirror of optical quality can be placed behind the lens, and the slit image photographed as before. For the Babinet-Bunsen type of instrument, if the angle of deviation cannot be reduced to zero, it may be necessary to remove the lenses and slit and set the system up for the test on an optical bench or a table. Modifications for particular cases will, in general, be easily devised.

While the Hartmann test is simple in interpretation and extremely searching, it has the limitation that it examines whole regions of the optics rather than one point at a time. The "knife-edge" test of Foucault[11] provides for detailed examination. The image of a pinhole or narrow slit is observed with the unaided eye placed close to the image, or with a low-power telescope focused on the lens. Since each point of the lens contributes to each point of the image, the lens should be seen filled with light. A knife-edge passed through the focal plane should cut all beams simultaneously and the whole lens should become dark suddenly and uniformly. Any remaining bright areas indicate imperfections or aberrations which cause the beam to be diverted from the true image. In practice, care must be taken to find the exact focal point; cutting the beam on either side of this point leads to a progressive darkening of the field from one side or the other. The knife-edge may conveniently be a safety-razor blade mounted on a micrometer screw. The interpretation of the knife-edge test requires some experience, which can be gained by the examination of lenses the condition of which is known. A good description of the procedure, with illustrations of the results of tests on lenses with various defects, will be found in Strong's *Procedures in Experimental Physics.*[12]

. It is clear that in the case of satisfactory optics the knife-edge test may be used to determine the focus, which is, as noted above, the plane in which the passage of the knife-edge darkens the whole field simultaneously. The method is, in fact, nearly as sensitive as the photographic procedure in determining foci for visible light. Because of its simplicity and speed, it may often be preferred. (See page 155.)

In the case of instruments manufactured under modern interferometric control, it is to be expected that tests such as those described above will show that the whole aperture of the optics is usable. Certainly no new instrument should be accepted if appreciable defects are disclosed. Older instruments may require that defective areas of the

[11] *Recueil des travaux de Leon Foucault*, p. 232, Paris, 1878; or *Mon. Not. R. Astr. Soc.*, **19**, 284, 1859.
[12] J. Strong, *Procedures in Experimental Physics*, p. 69. New York: Prentice-Hall, 1938. Also see H. G. Conrady, *Tr. Opt. Soc. Lond.*, **25**, 219, 1924; R. Kingslake, *Proc. Phys. Soc. Lond.*, **49**, 376, 1937.

optics be covered by screens before sharp lines can be obtained. It should be remembered that such diaphragming will reduce the illumination. While the resolving power should be improved, it will be less than the ideal if the net thickness of the prism is reduced, that is, if one edge of the prism is cut off (see page 61). If the illumination and resolving-power losses are significant, replacement of the defective parts may be advisable.

42. Influence of Slit Width and Mode of Illumination on Line Form and Intensity

The conditions which affect the flow of energy through a spectrograph have been discussed in Sections 18–24. The assumption there made was that the slit acted as a simple aperture in admitting light; that is, that there was no diffraction at the slit edges. However, as was seen in Section 17, there is diffraction at the main aperture diaphragm of the spectrograph and a resultant line image which is a diffraction pattern and not a simple geometrical image of the slit. The effect was shown to occur with an infinitely narrow self-luminous source. Actually, the slit cannot be infinitely narrow, and it is therefore very difficult to attain illumination which is the equivalent of self-luminosity (the so-called noncoherent mode), in which the phase relations of the light from each part of the slit are independent of those of every other part, and, consequently, rays from the various points of the slit reach every part of the collimator surface in a perfect mixture of phases. At the other extreme of slit illumination is the coherent mode, in which all rays reach the slit in the same phase. Neither of the modes of illumination is ordinarily exactly attained in practice, although they may be approximated.

The effect of finite slit width in the noncoherent mode of illumination was first discussed by Wadsworth,[13] whose work was corrected and extended by Schuster.[14] More recently, the whole problem has been handled theoretically by van Cittert[15] and by Münster,[16] among others, and experimentally by Stockbarger and Burns.[17]

Complete agreement among the various authors is lacking, especially in regard to the observable distinctions between the self-luminous and non-self-luminous cases. The attempts at verification of the theories seem, in general, complicated by experimental difficulties, and not wholly conclusive. The presence of lens aberrations and of optical inhomogeneities, which might completely obscure or alter the effects

[13] F. L. O. Wadsworth, *Phil. Mag.*, **40**, 137, 1897.
[14] A. Schuster, *Astrophys. J.*, **21**, 197, 1905.
[15] P. H. van Cittert, *Zeits. f. Phys.*, **65**, 547, 1930, and **69**, 298, 1931.
[16] C. Münster, *Ann. d. Phys.*, **15**, 619, 1932.
[17] D. C. Stockbarger and L. Burns, *J. Opt. Soc. Am.*, **23**, 379, 1933.

sought, does not usually appear to have been sufficiently considered. While further work remains to be done in this field, some of the fundamental facts about slit illumination and about the effect of slit-width variation seem well established and will be discussed.

With an infinitely narrow slit, as pointed out on page 30, the slit image is a simple diffraction pattern in which the intensity of the central maximum is zero. As the slit is opened, the intensity of the central maximum increases rapidly to a peak value, about which it thereafter fluctuates slightly, while the width of the line steadily increases. This is shown graphically in Fig. 46, which is taken from van Cittert. I_c
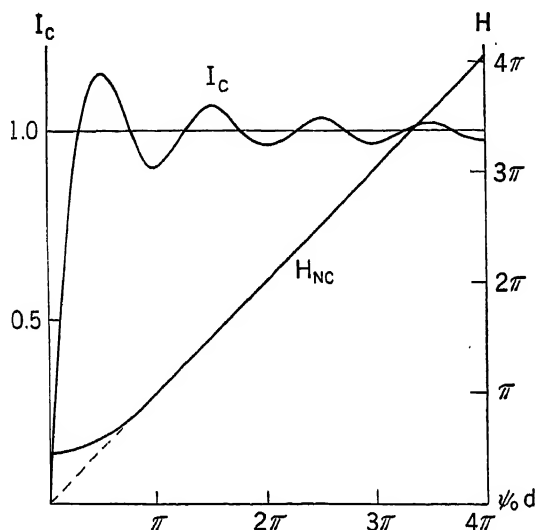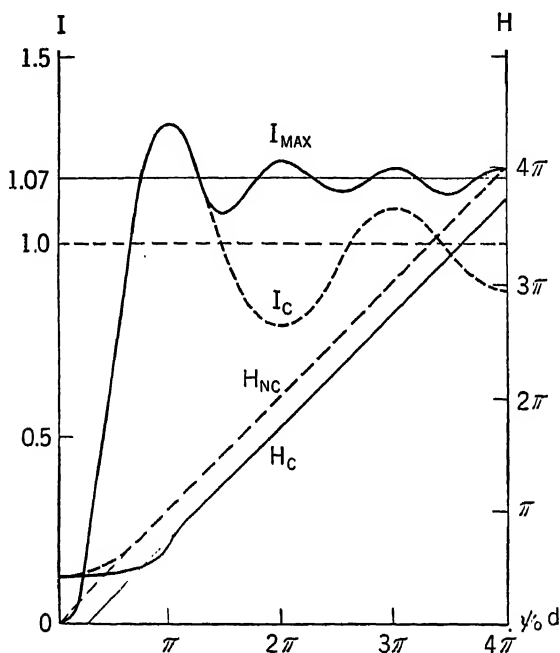

Fig. 46. Line Intensity and Width for the Noncoherent Mode of Illumination. Variation of central intensity, I_c, and line width, H_{NC}, according to van Cittert.

represents the central intensity of the first maximum in arbitrary units, while H is the half-width of the line (width from center to point where intensity has fallen to half). Both I_c and H are plotted as functions of the slit width. The slit width and line half-width are both expressed in terms of a parameter $\psi_0 d = \pi B d/\lambda f$, where B is slit width, λ the wave length used, f the focal length, and d the semi-diameter of the collimator lens. It will be seen that for $\psi_0 d = \pi/2$, the central intensity is a maximum, while the half-width is but little increased over that for an infinitely narrow slit. For wider slits, the central intensity oscillates slightly about its limiting value, while the half-width increases linearly directly with the slit width. In fact, the line image grows almost flat-topped, giving, with wider slits, a broader image of nearly the same sharpness of edge. Accordingly, unless for some reason a broad line image is desired, the maximum intensity and resolution are obtained

with a slit width such that $\psi_0 d = \pi/2$; whence $B = \frac{1}{2}\lambda f/d = \lambda f/D$, where D = diameter of collimator lens or aperture, or finally, $B = \lambda$ (f/-number). In the case of the large Bausch and Lomb spectrograph, for example, with quartz optics at 3500A, with $D = 70$ mm, and with $f = 1800$ mm, we find $B = .009$ mm.

Van Cittert's results are not entirely in agreement with those of Schuster. In particular, Schuster finds that the central intensity always increases as the slit is made wider. However, Schuster also concludes that a slit width $B = \lambda f/D$ is the best choice for a combination of good central intensity and negligible loss of resolving power. For a slit of width $\lambda f/D$, the central maximum of the diffraction pattern formed by the slit on the collimator lens is twice as wide as the lens. The actual width of the diffraction pattern of the slit formed by the camera lens depends on the focal length of the camera lens, as does also, of course, the size of the geometrical image which would be formed if there were no diffraction. With a slit of width $\lambda f/D$, the geometrical image is one-half as wide as the diffraction image—the distance between the first lateral minima on each side—for an infinitely narrow slit.

Van Cittert (*loc. cit.*) has calculated the effect of finite slit in the coherent mode of illumination, in which all rays from the slit are in the same phase. He finds that as the slit is opened, a flat-topped image is no longer obtained, but that a faint structure appears in the image with a multiplicity which depends on the slit width. The maximum intensity is not always at the center. Fig. 47 shows, from van Cittert's results, the variation of maximum intensity in the image, $I_{\max}$, of central intensity I_c and of half-width H_c as functions of $\psi_0 d$. The half-width for noncoherent illumination is shown for comparison. It is seen that $I_{\max}$ and I_c are both at a maximum for $\psi_0 d = \pi$. This slit width is double the optimum slit width in the noncoherent case, while the half-width of the line is very little wider than the minimum and somewhat narrower than in the corresponding noncoherent case.

The coherent and the noncoherent modes of illumination are limiting cases which are not exactly attained in practice. Truly coherent illumination requires a point source at an infinite distance from the slit; an approximation is a small spark or a capillary discharge used with no condensing lens and placed at a distance of five or more times the focal length of the collimator. Noncoherent illumination is approximated when an image of the source is formed on the slit or when a source large enough to fill the collimator aperture is placed before the slit. If loss of light by diffraction is to be avoided in the noncoherent case, the beam entering the slit should have a considerably larger aperture than the collimator.

In the use of any given spectrograph, if it is desired to attain the best resolving power with reasonable light intensity, or a flat-topped spectral

line of uniform blackness for photometric purposes, some investigation may be necessary to find the best slit width and illuminating system. To determine the best slit width in a given case, the optimum slit width for the limiting case can be calculated and tried, as well as wider and narrower ones. Such tests are well worth while. Slits wider than the experimentally determined critical width give lines which have little or no greater central intensity but are only wider and, perhaps, less uniform, while a narrower slit may result in a great loss in intensity

Fig. 47. Line Intensity and Width for the Coherent Mode of Illumination. Variation of maximum intensity, I_{max}, of central intensity, I_C, and of line width, H_C, according to van Cittert. The line width for the noncoherent mode, H_{NC}, is shown for comparison.

without gain in sharpness. It is also well to investigate the effect on sharpness and intensity of reducing the aperture of the entering beam to less than that of the collimator lens. Such reduction cuts down the contribution of the outer edges of the collimator; but since, because of diffraction, these are less strongly illuminated than the center, the loss of light may not be great. In some cases significant gains in the sharpness of the lines may result.

The preceding discussion has assumed ideal optical imagery and the absence of defects in the optics. In many spectrographs, however, the theoretical resolving power and line form may not be attained because of the imperfections of the optical system, which result in a broader

and less uniform line than that calculated from the theory. Some tests for the detection and localization of such errors have been described in Sec. 41. In the case of an imperfect instrument, a slit much wider than the optimum width may result in no appreciable increase in image width, while at the same time a much greater image illumination may be attained.[18] This failure of the actual resolving power to equal the theoretical is likely to be particularly noticeable in spectrographs of large camera aperture, which are likely to have noticeable residual aberrations. For any spectrograph, however, it is best to observe experimentally the effect of slit width on resolving power and intensity of illumination.

43. Light Losses in Spectrographs

In passing through any spectrograph, as through any optical instrument, light is lost through absorption in the lenses and prisms and through reflection at each surface in the optics. The first careful treatments of these losses in spectrographs were by Pickering[19] and by Wadsworth.[20] Little of importance has been added to their treatments.

In the case of loss by absorption, if I_0 is the intensity of the incident beam and I that of the transmitted beam, then by Lambert's law

$$I = I_0 e^{-kd} \tag{38}$$

where k is the absorption coefficient and d the thickness of material.

Then,

$$\log_e \left(\frac{I_0}{I} \right) = kd \tag{39}$$

Since $\log_{10} a = .4342 \log_e a$, this may be written

$$\log_{10} \left(\frac{I_0}{I} \right) = k'd \tag{40}$$

This form is often more convenient for calculation. Handbooks, such as the *Handbook of Physics and Chemistry* and the *International Critical Tables*, give values of the fraction of light transmitted at different wave lengths for given thicknesses of various materials. From these k' or k may be determined.

It should be noted that if I_0 and I are, respectively, the intensities entering the material and reaching the opposite surface, I/I_0 is called the *transmittance*. In practice, it is the intensity incident on the sample surface and that emergent from the other surface which are measured.

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[18] A. C. S. van Heel, *Revue d'Optique*, **12**, 49, 1933.
[19] E. C. Pickering, *Am. J. Sci.*, **45**, 301, 1868, and *Phil. Mag.*, **36**, 39, 1868.
[20] F. L. O. Wadsworth, *Astrophys. J.*, **2**, 264, 1895.

Their ratio is called the *transmission*, and this ratio takes into account not only absorption but also the reflection losses at the two surfaces. For normal incidence on a glass-air sample, the transmission is about 92 per cent of the transmittance. It is important, in using the tables, to observe which ratio is given.

For transparent materials, in regions not too close to the transmission limits, the transmittance of samples 1 cm thick is usually from 98 per cent to 100 per cent; accordingly, absorption losses are not large. As the regions of absorption are approached, the losses may become large and affect the choice of prism angle or length of face.

Pickering pointed out that for prisms of the same aperture and of the same material, the loss by absorption is the same for equal angular dispersion, regardless of the number of prisms used or of their refracting angles, that is, regardless of whether several prisms of small angle or fewer prisms of larger angle are used. This is true since, in the calculation of the transmittance by Equation (40), d is the average glass thickness, or half the base times the number of prisms, m. The average glass thickness is half the prism base. From page 60, this is

$$\frac{t}{2} = \frac{2a \sin \frac{\alpha}{2}}{\sqrt{1 - n^2 \sin^2 \frac{\alpha}{2}}}$$

or for m prisms,

$$m\frac{t}{2} = \frac{2am \sin \frac{\alpha}{2}}{\sqrt{1 - n^2 \sin^2 \frac{\alpha}{2}}}$$

But from Equation (33), the angular dispersion for m prisms is

$$\frac{d\theta}{d\lambda} = \frac{2m \sin \frac{\alpha}{2}}{\sqrt{1 - n^2 \sin^2 \frac{\alpha}{2}}} \cdot \frac{-c}{(\lambda - \lambda_0)^2}$$

Hence, for equal angular dispersions the transmittance depends only upon the material and aperture. Since the resolving power, by Equation (35), likewise depends on the glass thickness traversed, it follows that for a given material, equal resolving powers mean equal transmittances, for all prism arrangements.

There are, however, two ways in which the transmittance may be improved at the expense of resolving power. First, if the thick half of the prism is diaphragmed off, the amount of light incident on the prism is cut in half. The average thickness of glass traversed is also cut in

half, and since $e^{-.5} = .6$, there is a small relative gain in transmittance, although at the loss of half the resolving power. Second, a more important gain may be made by reducing the prism angle and sacrificing angular dispersion as well as resolving power.

Van Cittert[21] has pointed out that in the case of strong absorption, the spectral line shape changes, the lines becoming broader and having relatively less central intensity. Van Cittert gives the following data:

Transmittance	Central Intensity	Half-Width of Line
1............................	1.	1.
0.50.......................	0.475	1.04
0.25.......................	0.165	1.19
0.125......................	0.06	1.50
0.0625....................	0.015	3.

It will be noted that the central intensity decreases much more rapidly than the transmittance, while the increasing line width cuts down the resolving power. Accordingly, where the absorption is large there will be a gain in using a prism of smaller angle, since the smaller absorption will lead to greater central intensity, while the increase in resolution will partially offset the loss in angular dispersion. For example, van Cittert states that if a 60° prism which transmits only $\frac{1}{16}$ of the light is replaced by a 15° prism of the same material, the spectral lines will be one-third as wide and eleven times as intense, while the resolution will be 40 per cent of the original resolution. It does not appear that reflection losses have been considered. No experimental tests of these computations have been reported.

The reflection losses in an optical system may be calculated by the equations of Fresnel. If i and r are the angles of incidence and reflection, the fraction reflected at a surface of a light plane polarized at right angles to the plane of incidence is

$$X = \frac{\sin^2 (i - r)}{\sin^2 (i + r)}$$

while the reflected fraction of light which is plane-polarized in the plane of incidence is

$$Y = \frac{\tan^2 (i - r)}{\tan^2 (i + r)}$$

The transmitted amounts will be, respectively, $1 - X$ and $1 - Y$, and for an unpolarized beam the total transmission will be

$$T = \tfrac{1}{2}[(1 - X) + (1 - Y)]$$

[21] P. H. van Cittert, *Zeits. f. Physik*, **69**, 298, 1931.

The same calculation must be repeated at each surface; in particular after passing m surfaces with equal angles of incidence and refraction, as in a prism train,

$$T = \tfrac{1}{2}[(1 - X)^m + (1 - B)^m] \tag{41}$$

It should be noted that, since the two polarized components follow different laws, an unpolarized beam is more or less polarized by reflection. At the polarizing angle, when $\tan i = n$, $i + r = 90°$ and polarization is at a maximum. After several reflections the light is completely polarized. At this angle, T cannot be less than 50 per cent, and reflection losses will be at a minimum in a train of prisms. The necessary prism angle for maximum polarization of the ray at minimum deviation is 67°22′ for $n = 1.5$, 64°0′ for $n = 1.6$, and 60°56′ for $n = 1.7$.

Wadsworth (*loc. cit.*) has made extensive calculations, for one or more prisms and for different indices, of the effect of prism angle on loss of light, on length of prism face, on dispersion, on resolving power, on aperture, and on volume of prism. Many of the results are reproduced in Baly, Vol. I, Ch. III. As an example, the table below gives, for index 1.6, some comparisons of 60° prisms with prisms having the angle of maximum polarization, 64°. It will be seen that, with 64° prisms, the

TRANSMISSION AND DISPERSION OF PRISMS OF INDEX 1.6

Angle	Fraction of Light Transmitted				Angle of Incidence	Dispersion $d\theta/dn$ per Prism	Beam Aperture per Unit Base
	1 prism	*2 prisms*	*4 prisms*	*10 prisms*			
60°	0.853	0.748	0.618	0.491	53°8′	1.667	0.600
64°	.818	.702	.582	.505	57°59′	1.999	.500

loss of light by reflection increases but little after the fourth prism. Prisms of small angle have less loss of light in a single prism than prisms of large angle, and have a larger beam aperture per unit of base. They are inferior, however, in dispersion and in resolving power. For a given lens aperture and a given resolving power, it is best, except in the case of special requirements such as the need for high dispersion, minimum volume, and so forth, to choose prisms of the angle for maximum polarization. Since, as seen above, this choice calls for prisms with a refracting angle only slightly over 60°, the greater ease of grinding 60° prisms makes that angle the most common choice.

For the case of normal incidence, $i = r = 0$, both Fresnel formulae for the intensity of the reflected light take the form

$$X_0 = Y_0 = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2$$

where n_1 and n_2 are the indices of the two media. If one medium is air,

$$X_0 = \left(\frac{n - 1}{n + 1}\right)^2$$

The fraction of light transmitted by m similar surfaces is then $T_0 = (1 - X_0)^m$. For an air surface, with an index in the other medium of 1.5, $X_0 = .04$; in other words, 4 per cent of the light is lost by a reflection at normal incidence. For angles even as large as 30°, the results computed by the Fresnel equations for oblique incidence differ but little from those obtained by the expressions for normal incidence. Except in cases of very divergent beams or of a lens of very sharp curvature, the simpler expressions for normal incidence are adequate for calculating the transmission of lenses and windows. For a cemented interface between two different materials, the expression for X_0 is

$$X_0 = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2$$

The loss is much smaller than at an air surface. Lens designers, therefore, attempt whenever possible to use cemented surfaces in compound lenses.

It has long been known that the reflection losses at tarnished glass surfaces are less than at freshly polished ones. Recently C. H. Cartwright[22] has pointed out that the effect may be produced by evaporating a thin film of lithium fluoride on the lens surface. If the thickness is properly chosen, interference between the beams reflected at the fluoride and at the glass surface will destroy the reflection over a considerable wave-length range.

The reflection losses in a spectrograph may be large. For example, calculations have been made in the Physical Laboratory of the University of Michigan on the transmission of a system consisting of a quartz monochromator with simple quartz lenses and a Young-Thollon prism system combined with an illuminating system of two quartz-fluorite cemented achromats and a quartz window. There are reflections at normal incidence at two fluorite-air, ten quartz-air, and two quartz-fluorite surfaces, and oblique reflections at two quartz-air prism surfaces. The calculated transmission varies from 39 per cent at 2194A to 44 per cent at 4341A.

If the radiation is continuous rather than monochromatic, an additional effect, sometimes called the *slit-width effect*, must be considered in

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[22] C. H. Cartwright, *J. Opt. Soc. Am.*, **30**, 110, 1940.

calculating the relative energy transmitted at different wave lengths by spectrographs or monochromators. Spectral lines are monochromatic images of the spectroscope slit. Accordingly, a continuous spectrum is formed by an infinite array of overlapping images. The amount of overlapping varies inversely with the linear dispersion $dx/d\lambda$. But

$$\frac{dx}{d\lambda} = f\left(\frac{d\theta}{d\lambda}\right) \tag{1}$$

and if the lens is a simple lens, uncorrected for chromatic aberration,

$$\frac{1}{f} = (\mu - 1)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \text{ or } f \propto \frac{1}{\mu - 1}$$

and the slit-width correction

$$S \propto \frac{\mu - 1}{d\theta/d\lambda}$$

$d\theta/d\lambda$ can be calculated as described in Sec. 29. For the quartz monochromator mentioned above, this factor S varies from 1.00 at 2265A to 6.31 at 3961A; that is, the spectrum overlapping is 6.31 times as great at 3961A as at 2265A.

Finally, if relative energies are to be compared in different regions with an instrument using lenses which are not chromatically corrected, it should be remembered that the aperture of the instrument changes, since the focal length of the lenses changes with wave length. If the system is always filled with radiation, the radiant energy per unit area in the spectrum is inversely proportional to f^2 (Sec. 25). Thus the focal-length correction $\propto (1/f^2) \propto (\mu - 1)^2$. The effect for quartz varies from 1.00 at 2265A to 1.23 at 3961A.

44. Stray Light in Spectrographs

Stray light may reach the photographic plate in a spectrograph by virtue of:

1. Leakage of light through the housing and plate holder.   .
2. Reflection and scattering of light from the walls and from the mountings of the optics.
3. Reflection and scattering of light at the surfaces of the optics.
4. Scattering of light and fluorescence within the optics.

Stray light from any cause may produce either a general or a localized fogging of the spectrograms. This fogging is always troublesome if the plates are to be measured; it should be reduced to an imperceptible amount if photometric work is to be done on the plates. In a well-designed instrument, attention will have been paid to stray light. It is

desirable, however, in placing orders for spectrographs, to include specifications on the permissible amount of stray light, and it is wise to make some tests on any spectrograph which is to be used for research.

Light leakage may result from the warping or cracking of wooden housings and plate holders or from the failure to make joints and plate-holder ways tight in wood or metal housings. A check of light-tightness should be made and any leaks stopped, since it should always be possible to use a spectrograph in a lighted room without precaution against light leaks. A simple check can be made if the operator, with a black cloth covering his head, looks into the plate-holder opening while an assistant carries a strong light, such as a 500-watt electric bulb, about the spectrograph; almost any significant leak will be revealed. Leaks in the plate holder, in its ways, and in the dark slides are not detected by this test. To check against them, a plate can be placed in the plate holder, the dark slide drawn, and a 500-watt bulb moved about the plate holder. If there are no leaks, the plate will be fog-free on development. Such leaks as are found can usually be stopped by simple remedies. For leaks and cracks in wooden cases the gummed sponge-rubber strips sold for stopping automobile rattles are often useful. Felt is to be avoided, especially for sealing such moving parts as plate-holder ways and dark slides. The lint which is sure to be released is likely to settle on the optics or plate and to cause trouble. Velvet or rubber is better, but with well-made parts of metal or fiber little of either should be needed.

Reflection and scattering of light from the walls and mountings cannot be prevented but can be reduced in amount and effect. On the collimator side, some excess light always arises from the usual overfilling of the optics by the entering beam. On the camera side, if the whole range of spectrum dispersed by the prism is not accepted by the plate, the red or violet ends which fall off the plate must be prevented from contributing to plate fog by reflection or scattering. Usually, however, this light can be almost wholly prevented from reaching the plate by suitable baffles and absorbers.

If in the spectrograph the collimator and camera are separate, as in the Babinet-Bunsen type, the collimator should be examined first for wall reflections. It should be removed from the instrument or a mirror arranged to permit a view down the tube. With a strong light before the wide-open slit, reflections from the wall are readily seen. They can usually be stopped by a series of diaphragms which increase in aperture from slit to lens and which are so designed that each permits every point of the slit to be seen from every point of the lens. The diaphragms can thus occupy the space in the collimator outside the planes VV' and HH'. A simple geometric sketch based on the law of reflection will usually indicate quickly the required number and position of stops to cut off all excess light. The diaphragms should be blackened,

and should also be sharpened to avoid edge reflection. A little black velvet may be necessary to stop reflections at or near the lens mountings.

Similarly, diaphragms must be placed in the camera to stop light reflected from the side walls. If this light is in the visible region, it can be seen at the plate-holder slot when a strong light is placed before the wide-open slit. For the invisible infrared or ultraviolet, some calculation of emergent wave lengths and angles, together with a scale drawing of possible reflections, may help. Or, if the prism can be rotated, the visible spectrum may be thrown on either side of the housing and its reflection observed. Because of the large size of the camera lens and plate holder, it is often more difficult to stop all reflected light in the camera than it is in the collimator. The problem is usually simpler if the camera housing is somewhat larger than the bare minimum required to include the full plate-holder beam.

Reflections present somewhat more difficulty in the Littrow type of spectrograph than in the Babinet-Bunsen type, because the entering and dispersed beams travel in the same housing, and more restrictions are thereby placed on the location of diaphragms. Here, again, it is helpful to have a case of generous size; usually a few well-placed diaphragms will then sufficiently reduce the fogging due to wall reflections.

After wall reflections have been eliminated, the observer, with an eye placed at the plate-holder slot just above or between the spectral lines, should see no light in the direction of the camera lens. Ordinarily, however, light reflected from the prism and lens surfaces will be seen. In the Babinet-Bunsen instrument, the reflections arise from light which, after passing through the prism, has been reflected from one of the lens surfaces just as from a spherical mirror, and also, except for first surface reflections, refracted by passage through the lens before or after reflection. These reflected rays, since they are dispersed light, form at their focus small spectra which may be real or virtual images before or behind the lens. If the rays after reflection can strike the photographic plate, fogging will result, as in the case of the flare spot in Fig. 27. In carefully designed camera lenses, the secondary spectra formed by reflections will be focused so far from the plate that their light on reaching the plate will be spread out, and so will cause little trouble.

Like the wall reflections, the lens reflections which arise in the Littrow-type spectrograph are more troublesome than in the straight-through type of instrument, because reflections of the entering beam are thrown back toward the plate. Inspection from the rear will usually show two or more slit images and two or more spectra formed by reflection. Those which are between the lens and the plate are troublesome. They are easily identified by the observer if he looks at the camera lens while moving his head slightly from side to side; images in front of the lens will appear to move in the direction opposite to that of the motion of the

eye; those behind will appear to move in the same direction. Ordinarily, the slit and plate are in the same horizontal plane; the images will then be in this plane and can be blocked by a narrow opaque strip across the center of the lens or by a small screen at the image point. Unless it is established that the energy distribution to the various parts of the spectrum is uniformly affected by these devices, they should not be used in photometric work where no condensing lens is used or where the source is imaged on the optics. An alternative is to tilt or turn the lens slightly to throw the reflection above or to one side. Only a few degrees of tilt or twist are permissible; otherwise, the astigmatism introduced would damage the perfection of the image.

Littrow spectrographs are sometimes seen with the plano-convex lens usual in such constructions mounted with the plane side toward the prism. Not only is this setting much worse than the reversed one in the
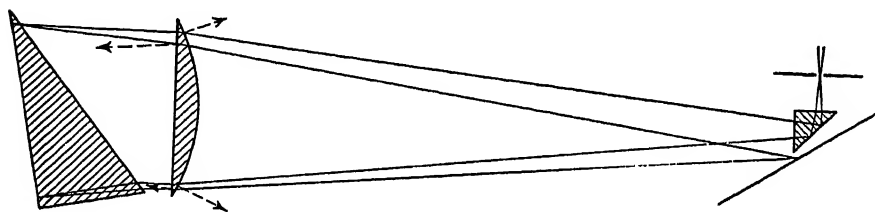
Fig. 48. **Reflections from Lens of Littrow-Type Spectrograph.** Plane surface of lens is toward prism.

amount of spherical aberration, but it leads to troublesome reflections (Fig. 48). Light reflected from the convex first surface diverges as from a virtual source at a distance $[(n - 1)/n]f$, or about $f/3$ behind the lens; hence this beam is so divergent that it cannot be kept off the plate by any reasonably small lens tilt or twist. The light striking the plane second surface is a parallel beam, and so any reflected light retraces its path and produces a slit image at the focal distance of the lens. If this strikes the plate, a bad flare spot is produced. A case has been seen where this slit image actually was formed on the polished rear surface of the slit, acted as a second slit beside the first, and produced on the photographic plate false spectra in focus and slightly displaced from the true spectra. Further difficulty arises from the fact that light, after dispersion by the prism, strikes the plane lens surface and is sent back through the prism again. Since this reflected beam is parallel, it will also be focused on the plate, and cases have been seen where this doubly dispersed spectrum has appeared mixed with the true spectrum.

An arrangement similar to that in Fig. 48, but with the lens reversed, will show much less troublesome reflections if a construction of the reflected rays is made. The beam reflected from the plane first surface is so narrow that it is easily diverted by a slight lens twist; the beam

reflected from the concave second surface converges to a real image and is easily blocked by a very small screen; the reflections of the dispersed beam from the prism are too divergent to be focused after a second dispersion in such positions as to cause trouble.

After wall and lens reflections have been disposed of, the observer, with his eye at the exit slot of the spectrograph but above or between the spectral lines, should see no light from the optics. Ordinarily some light is seen scattered by dust particles and scratches on the optical surfaces, and by bubbles and inhomogeneities in the optics. If short-wave-length ultraviolet light is involved, some samples of quartz and fluorite may show a faint fluorescence. Little can be done to suppress any of this stray light except that scattered by surface dirt. The lens and prism surfaces can be dusted with a camel's hair brush, washed, and polished with a soft cloth. For washing, ethyl acetate is useful. It is a good solvent and less likely than ether or alcohol to leave a greasy film or residue.

The final test which assures the satisfactory elimination of stray light is that, under illumination conditions much more severe than those likely to be met in practice, a photographic plate does not show visible fog. With a rapid plate, a wide slit, and a 5-ampere iron arc or other suitable light source condensed on the slit, an exposure should be made which, for the spectrograph used, is at least ten times that needed for a good spectrogram. If the plate, after processing, shows no signs of stray light or fogging, it can be reasonably assumed that trouble from this source will not arise.

45. The Effect of Temperature and Pressure on Prism Spectrographs

Changes in temperature and pressure may lead to serious difficulties in prism spectrographs through broadening and shifts of spectral lines and changes in focus. The temperature coefficient of the index of refraction of optical materials has already been noted (Sec. 34). It ranges from low positive values of the order of from 1×10^{-6} to 7×10^{-6} for various glasses to negative values as high as 8×10^{-4} for carbon bisulphide. The shift in spectral-line position due to changes in index of refraction may be determined by a comparison of dn/dt with $dn/d\lambda$ (see page 58). Thus, for flint glass, dn/dt is about 5×10^{-6} while $dn/d\lambda$ is 7 to 10×10^{-6}, and so

$$\frac{d\lambda}{dt} = \frac{dn/dt}{dn/d\lambda} = .7 \text{ to } .5 \text{ angstroms per degree}$$

For carbon bisulphide, $dn/dt = 8 \times 10^{-4}$, $dn/d\lambda = 17 \times 10^{-6}$, and $d\lambda/dt = 47$ angstroms per degree. Shifts of several angstroms per degree can certainly not be neglected, and even shifts of a fraction of an angstrom

per degree can cause serious losses in definition and resolving power in instruments of high dispersion.

The shifts due to temperature will cause serious changes in focus for nonachromatic instruments in which the photographic plate makes an angle with the optical axis. The shift increases as the angle becomes smaller and is therefore of considerable importance in work with single-prism quartz spectrographs, where the angle may be as small as 25°. Furthermore, the change in index of refraction will affect the focal length of the collimator and camera lenses, and the expansion of the spectrograph bed and mountings with a rise in temperature will alter the spectrograph dimensions.

For most crystalline materials, the temperature coefficients of expansion are different in the direction of the different crystal axes. Where such are used, change of temperature will alter the prism shape and angle. The effect on the spectrum of a small change in prism angle is a change in dispersion, as is the effect of a small change of index. In fact, if dn/dt is determined from measurements on the prism, the effect of $d\alpha/dt$ will be included in the result unless precautions are taken to eliminate it.

Optical materials are all poor thermal conductors; hence considerable time is required for the whole volume of a prism to reach thermal equilibrium following a change in the surrounding temperature. Until equilibrium has been attained, the temperature gradients in the prism lead to variations in the index of refraction and consequent loss of line definition. Merton[23] found that if the prism is mounted in good thermal contact with the metal base and is covered, except for the refracting face or faces, with a close-fitting metal box attached to the base, the gradients are rendered so uniform that they do not noticeably impair definition. During long exposures, thermal control of the prism end of the spectrograph by insulation and by thermostatic regulation was found necessary to insure freedom from line shift due to temperature change.

Barometric pressure changes, with resultant variations in the index of refraction of air, can likewise cause shifts in line position. As Merton pointed out, at normal temperature and pressure, the change in the index of refraction of air is 3.6×10^{-6} per centimeter change in pressure, which, if $dn/d\lambda$ is 9×10^{-6}, as in flint glass, leads to a shift of about .4A per cm change. Elliot and Cameron[24] have given data on a large three-prism Littrow-type spectrograph, with dispersion ranging from 12.5A/mm at 6000A to 2.5A/mm at 4000A, for which the displacement due to barometric pressure is .063 mm/cm-change in the middle of the visible region.

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[23] T. R. Merton, *Proc. Roy. Soc.*, **113A**, 704, 1927.
[24] A. Elliot and W. H. B. Cameron, *J. Sci. Inst.*, **14**, 28, 1938.

Changes of as much as 1 cm in barometric pressure are extreme, but changes of a millimeter or two during a long exposure can be expected. For instruments of high dispersion some precautions must be taken, unless exposures are to be made after a study of the weather forecasts. Elliot and Cameron enclosed their spectrograph in an airtight iron box maintained at a pressure of about 70 cm of mercury. Merton placed a plane-parallel glass plate behind the slit of his spectrograph, and rotated it manually to introduce apparent displacements of the slit to counterbalance the effect of pressure changes which were observed in barometric readings. Beutler and Fred,[25] in a large grating instrument, made this compensation automatic by linking such a plane-parallel plate to an aneroid barometer (see page 179).

The effects of temperature and pressure changes are most important for large spectrographs and for long exposures. They can, however, lead to annoying losses of definition in other cases. Most spectrographs will require a change in focus as the change in seasons alters the normal temperature of the laboratory.

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[25] H. Beutler and M. Fred, *Phys. Rev.*, **57**, 69, 1940.

CHAPTER 6
The Diffraction Grating: Theory and Production

The diffraction grating, discovered by Fraunhofer, and brought to a more perfect stage by Rowland and by Michelson, has played an important role as a dispersing device, replacing the prism for this purpose in many applications. In the ultraviolet below 2000A and in the infrared, where no transparent media for prisms are known, it is indispensable; in the visible region, the great dispersion and resolving power attainable give it a unique position. Probably only the small number of machines for producing gratings, the difficulties of ruling, and the consequent high cost and scarcity of good gratings, have restricted the use of this instrument.

46. The Plane Grating

The theory of the diffraction grating has been developed and presented excellently by Rowland[1]; it is fully discussed by numerous authors.[2] Accordingly, only an elementary treatment will be given here. It has been shown (Sec. 17) that the image of a slit formed by light which has passed through an aperture of width b is a diffraction pattern, and that the width of the first maximum is $2f\lambda/b$. The width of the maximum is, then, inversely proportional to b; and if b is so small as to be of the order of magnitude of λ, the maximum may become so wide as to cover the whole field of view. A diffraction grating is made up of an array of such narrow slits, parallel, equidistant, and close together. In the transmission grating, light passes through these slits or openings; in the reflection grating, the light is reflected from close parallel grooves or rulings on a surface, and these rulings act as individual slits. In either case the behavior is fundamentally the same, and the transmission grating may be taken as an example.

The effect of the width b of the individual rulings will be considered later, but it will be assumed here that the width is so narrow that the central diffraction maximum fills the entire field. In this wide central maximum are found new maxima and minima arising from interference

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[1] H. A. Rowland, *Phil. Mag.* (5), **35**, 397, 1893; *Astronomy and Astrophys.*, **12**, 129, 1893.
[2] R. W. Wood, *Physical Optics*, 3rd. ed., Ch. 7; Meyer, *Diffraction of Light, etc.*, Ch. 6.

between beams passing through the individual slits. With many slits or openings, these new maxima become very sharp, and they are narrow compared to the minima or distances between the maxima. It is these maxima which constitute the spectra of the grating. Their position is readily determined. In Fig. 49, $ABCDE$ represents a section of a plane transmission grating, where BC and DE are two adjacent openings and AB and CD the opaque strips between, which are not, in general, of the same width as the slits. The slits, however, must all be of equal width and spacing. A beam of parallel rays, $L_1L_2L_3$, as from a collimator, is incident on the grating at an angle α with the grating normal. After passage through the grating, diffracted light moves out from each opening
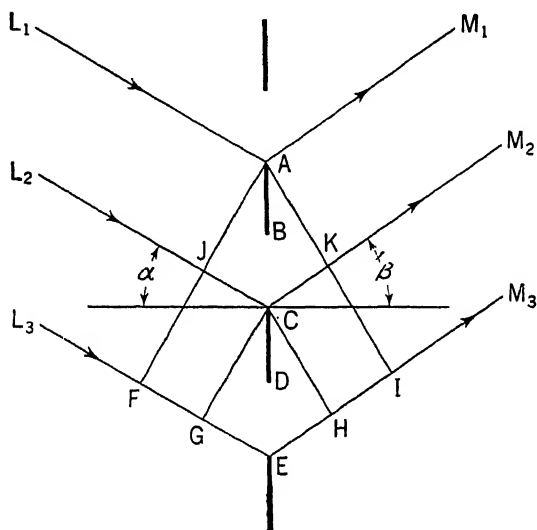
Fig. 49. Diffraction by a Plane Transmission Grating.

in all directions, since the openings have been assumed to be sufficiently narrow.

Consider first the beam, $M_1M_2M_3$, diffracted at an angle β with the normal. In the incident beam, the rays $L_1L_2L_3$ are at A, J, and F, respectively (on the perpendicular to the rays at A), in the same phase—AJF is a plane wave front. Likewise, the points AKI are in the same phase, or on a plane wave front in the diffracted beam. The beam L_2M_2 has, however, traversed a path greater than the beam L_1M_1 by the distance JCK, while the beam L_3M_3 has traversed a path greater by FEI. It is apparent from the figure that $FEI = 2JCK$, and that the path differences for succeeding grating openings will increase in arithmetical progression. If the rays $M_1M_2M_3$ are brought to a focus by the objective lens, and if, for light of any wave length, JCK is a whole wave length λ or integral multiple thereof, the rays of that wave

length will reinforce one another and produce a bright image of the source. Therefore, if the grating space $AC = d$, it follows from the figure, as the condition for a bright maximum, $JC + CK = d(\sin \alpha + \sin \beta) = n\lambda$. A succession of spectra will also appear on the other side of the direct beam ($\beta > -\alpha$). For these spectra it is easily seen that CK is greater than, and opposite in sign to, JC. The expression $d(\sin \alpha + \sin \beta)$ will then be negative. Since d, λ, and α can always be defined as positive, n is taken as negative for the spectra on the other side of the direct beam. The complete expression for the image position is accordingly:

$$\pm n\lambda = d(\sin \alpha + \sin \beta) \tag{42}$$

where β may be negative and n will then become negative for $|\beta| > |\alpha|$. This equation holds for all values of α and β, and for reflection as well as transmission gratings. For reflection gratings, $\sin \alpha$ and $\sin \beta$ will have opposite signs if they are on opposite sides of the grating normal; n will be negative if α and β are on opposite sides of the direct reflection.

Equation (42) is the fundamental grating equation for the position of the diffracted images. The successive images formed for $n = \pm 1$, ± 2, ± 3, and so forth, are called the images of the first order, second order, and so on. The images of different wave lengths will be formed for any fixed n at different angles β, giving spectra of different orders. It will be noted that, contrary to the prismatic spectrum, in a grating spectrum the shortest wave length is least deviated.

47. Dispersion of a Grating

An expression for the angular dispersion of a grating may be readily obtained by differentiating Equation (42). Assuming α to be constant, that is, a fixed slit, $n \cdot d\lambda = d \cdot \cos \beta d\beta$ or

$$\frac{d\beta}{d\lambda} = \frac{n}{d \cos \beta} \tag{43}$$

It will be seen that the dispersion is a minimum when $\beta = 0$, and the spectrum is observed on the normal to the grating. For this so-called normal spectrum, $d\beta = (n/d)d\lambda$, or, for small changes in wave length, $\Delta\beta = \text{const} \cdot \Delta\lambda$, approximately, and the dispersion is a constant and λ is a linear function of β. For gratings with 6000 and 12,000 lines per centimeter, approximately 15,000 and 30,000 lines per inch, the normal dispersion ($\beta = 0$) is $n \cdot 6000$ and $n \cdot 12,000 \times 10^{-8}$ radians per angstrom, respectively. These figures may be compared with those given for prisms on page 59.

A characteristic feature of gratings is the overlapping of spectra of different orders. It will be obvious from Equation (42) that for fixed values of α and β, if a wave length λ is observed in the first order

($n = 1$), there will also appear, at the same β, wave lengths of higher-order spectra such that $\lambda_1 = 2\lambda_2 = \cdots n\lambda_n$, and that the relation holds: $\lambda_2 = \lambda_1/2$, $\lambda_3 = \lambda_1/3$, $\cdots \lambda_n = \lambda_1/n \cdots$. Or, for example, the spectra of 9000A in the first order, 4500A in the second, and 3000A in the third are observed at the same angle. These overlapping orders can often be separated by the use of filters which pass only limited wavelength regions, or by taking advantage of the limited spectral sensitivity of various photographic plates. On the other hand, it is often an advantage to photograph spectra of different orders simultaneously, so that known wave lengths in one region may be used to determine wave lengths in another region. The dispersion will be treated in more detail later (Section 52).

48.   Resolving Power of a Grating

The expression for the resolving power of a grating is readily obtained from the considerations of Sec. 17. AD (Fig. 50) represents a grating from which emerge two just-resolved beams of wave length λ and $\lambda + \Delta\lambda$, with wave fronts AC and AB, respectively. These beams, according to page 33, must differ in emergent angle by $\Delta\beta = \lambda/AB$, where AB is the beam width. By Equation (6),
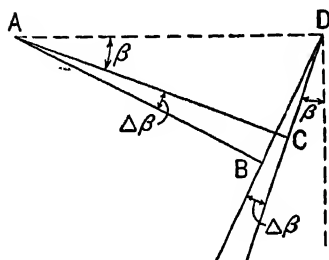
$$\frac{\lambda}{\Delta\lambda} = \frac{\lambda}{\Delta\beta} \cdot \frac{d\beta}{d\lambda} \qquad (44)$$

Fig. 50.   Diffraction by a Transmission Grating. The two beams are just resolved.

But $AB = AD \cos \beta = Nd \cdot \cos \beta$, where N is the number of lines in the ruled surface and d the grating space. Also, from Equation (43), $d\beta/d\lambda = n/(d \cos \beta)$. Making these substitutions in the equation for $\lambda/\Delta\lambda$,

$$\frac{\lambda}{\Delta\lambda} = Nd \cos \beta \frac{n}{d \cos \beta} = nN \qquad (45)$$

The resolving power of a grating, in this formulation, depends only on the product of the order and the number of rulings, and not on the wave length or grating spacing. To resolve the sodium D lines in the first order, the required resolving power is $\lambda/\Delta\lambda = 5893/5.967 = 987$; a grating with 987 ruled lines will have this theoretical resolving power. For a grating with 30,000 lines per inch, less than one millimeter of ruling would be required. Very large theoretical resolving powers, which, in fact, are closely attained in practice, may be reached in the higher orders of large diffraction gratings. Thus, A. A. Michelson[3]

[3] A. A. Michelson, *Studies in Optics*, p. 102. Chicago: University of Chicago Press, 1927.

describes the resolution of the green mercury line, λ5461, in the sixth order of a plate grating with 10-inch ruled surface. The theoretical resolving power, nN, is 660,000; the actual resolving power attained is 600,000.

Equation (44) represents the resolving power in terms of physical optics. Another aspect of the same facts, which is related to Heisenberg's "uncertainty principle," may be mentioned, since it helps in judging the effectiveness of different gratings. If the width AD of the grating is called w, then (from Figure 50) $\Delta\beta = \lambda/AB = \lambda/(w \cdot \cos \beta)$. This value is introduced into Equation (44), and Equation (43) is used, as follows:

$$\frac{\lambda}{\Delta\lambda} = \frac{\lambda \cdot w \cdot \cos \beta}{\lambda} \cdot \frac{d\beta}{d\lambda} = w \cdot \cos \beta \frac{n}{d \cdot \cos \beta} = \frac{w \cdot n}{d}$$

From Equation (42),

$$\frac{n}{d} = \frac{1}{\lambda} (\sin \alpha + \sin \beta)$$

whence,

$$\frac{\lambda}{\Delta\lambda} = \frac{w}{\lambda} (\sin \alpha + \sin \beta) \qquad (46)$$

In this formulation, the resolving power is determined by w/λ, that is, the number of wave lengths, λ, that are contained in the width w of the grating, and by the angles α and β. Higher orders of the same wave length λ appear, of course, at larger angles, thus increasing α and β, and therefore $\lambda/\Delta\lambda$. But different gratings that have the relation one to two in their grating spacings d, will show the second or first order, respectively, of the same wave length at the same angles. The resolving powers of both will then depend only on the ratio of their respective widths; their resolving powers will be equal if the widths are equal. For obtaining a high resolving power, the ruled surface must be wide; the smaller grating constant merely eliminates the overlapping of orders.

The geometrical meaning of the formula (46) is clear; it represents the path difference of the two extreme light rays that strike the grating, expressed in units of the wave length. This meaning is identical with the geometrical interpretation of the resolving power of a prism.

It may be observed that the existence of the resolving power of a grating is related to the fact that the image of the slit in monochromatic light is a diffraction pattern, as shown in Fig. 7, with minima and secondary maxima, and that the distance from the principal maximum to each of the first minima is determined by the value of $\lambda/\Delta\lambda$. The angle subtended between the maximum and first minimum (on either side) is, using Equation (44), as follows:

$$\Delta\beta = \Delta\lambda \cdot \frac{d\beta}{d\lambda} = \Delta\lambda \cdot \frac{n}{d \cdot \cos \beta} \qquad (47)$$

Here, the angular dispersion is used; the length, Δp, the projection of the angle $\Delta\beta$ on the plate, can be obtained by using the linear dispersion:

$$\Delta p = \Delta\lambda \cdot \frac{dp}{d\lambda} \qquad (48)$$

The relations between angular and linear dispersion are derived in Section 52, for plane and for concave gratings.

49. The Concave Grating

Like the prism, the plane grating requires the use of lenses or mirrors to collimate and to focus the incident and emergent light. It occurred to Henry Rowland to investigate whether a grating could not be ruled on a concave mirror, and the concave mirror used to focus the spectra formed by the grating. Such a "concave grating" proved, indeed, possible. Its use reduces the spectrograph to three parts—a slit, a concave grating, and the photographic plate. Moreover, the problem of chromatic aberration disappears, although the errors of the concave mirror, and especially astigmatism, cannot be disregarded. Above all, absorption by the lens materials is avoided; only one loss by reflection —at the grating itself—occurs. Accordingly, it has made possible investigations in regions of the extreme ultraviolet and infrared which previously were inaccessible because of the lack of transparent optical media.

Rowland announced his discovery in 1882 and in the next year gave the theory of image formation of the grating and of his mounting.[4] He showed that the rulings should be so spaced on the spherical surface as to be equidistant on the chord of the circular arc; that is, the spherical surface lies flat and is ruled as a plane grating is ruled, with equal relative displacement of ruling diamond and surface for each ruling stroke. Then, as Rowland showed, the same grating Equation (42) holds as for the plane grating, and the slit, grating, and spectra all lie on a circle whose diameter is equal to the radius of curvature of the concave gratings— the Rowland circle. The grating, of course, does not fit this circle, but is tangent to it at one point only. Later contributions to the theory of the concave grating were made by Glazebrook,[5] Mascart,[6] Baily,[7] and especially Runge.[8] The use of the concave grating in grazing incidence has been investigated by Mack, Stehn, and Edlen.[9]

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[4] H. A. Rowland, *Phil. Mag.*, **13**, 469, 1882; **16**, 197 and 210, 1883.

[5] R. T. Glazebrook, *Phil. Mag.*, **15**, 414, 1883.

[6] E. Mascart, *Jour. de Physique*, **2**, 5, 1883.

[7] W. Baily, *Phil. Mag.*, **22**, 47, 1886.

[8] Runge's theory is given in Kayser, *Handbuch d. Spectroscopie*, Vol. I, pp. 450–470; also C. Runge and K. W. Meissner, *Hand. d. Astrophysik*, Vol. 1, pp. 235–257.

[9] J. E. Mack, J. R. Stehn, B. Edlen, *J. Opt. Soc. Am.*, **22**, 245, 1932.

The elementary theory of the grating given here considers only a section through the grating in the plane of the Rowland circle. It neglects the effect of the length of the rulings and the failure of the grating to fit the Rowland circle rather than to be tangent to it; that is, it does not consider the effect of finite size of grating. In Fig. 51, AB represents a section of a concave grating, where A and B are two consecutive rulings, and the distance $AB = d$ the grating space. C is the center of curvature of the grating surface; S is a source of light. Light rays SA and SB, of wave length λ, incident at angles α and $\alpha + d\alpha$ after diffraction at the grating at angles β and $\beta + d\beta$, are brought to a focus at P. The angles subtended at C, S, and P by AB are $d\gamma$, $d\sigma$, and $d\rho$, respectively. SB is extended to G so that $SG = SA$; and PB is extended to F so that $PF = PA$. The condition for the rays SA and
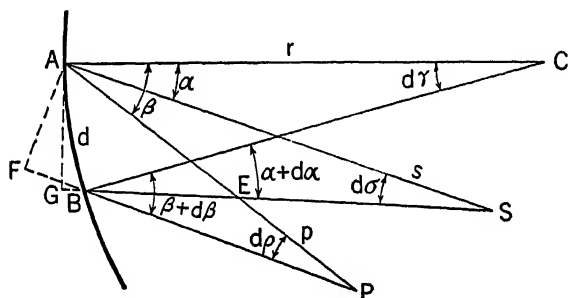
Fig. 51.   Diffraction by a Concave Grating.

SB to reinforce each other on reuniting at P, is that their light paths differ by an integral number of wave lengths, that is,

$$n\lambda = (SA + AP) - (SB + BP) = (SG + FP) - (SB + BP) = BG$$
$$+ BF = AB \sin \alpha + AB \sin \beta = d(\sin \alpha + \sin \beta)$$

Thus the concave grating obeys the same equation for position of the diffracted images as does the plane grating. By exterior angles,

$$\alpha + d\gamma = d\sigma + \alpha + d\alpha; \, d\alpha = d\gamma - d\sigma$$

and,
$$\beta + d\gamma = d\rho + \beta + d\beta; \, d\beta = d\gamma - d\rho$$

Also,
$$d\gamma = \frac{d}{r}; \, d\sigma = \frac{d}{s} \cos \alpha; \, d\rho = \frac{d}{p} \cos \beta$$

Differentiating Equation (42),

$$0 = \cos \alpha \, d\alpha + \cos \beta \, d\beta$$

Substituting the expressions above,

$$\cos \alpha \left(\frac{d}{r} - \frac{d}{s} \cos \alpha \right) + \cos \beta \left(\frac{d}{r} - \frac{d}{p} \cos \beta \right) = 0 \qquad (49)$$

or
$$\frac{\cos \alpha}{r} - \frac{\cos^2 \alpha}{s} + \frac{\cos \beta}{r} - \frac{\cos^2 \beta}{p} = 0 \qquad (49A)$$

It is clear that if expression (49) is to be satisfied for all values of α and β, the expressions in parentheses must be zero, since $\cos \alpha$ and $\cos \beta$ are neither always zero nor always in a constant ratio. Then,

$$\left. \begin{array}{l} \dfrac{d}{r} = \dfrac{d}{s} \cos \alpha \text{ or } s = r \cos \alpha \\[2mm] \dfrac{d}{r} = \dfrac{d}{p} \cos \beta \text{ or } p = r \cos \beta \end{array} \right\} \qquad (50)$$

and

These are the polar equations for a circle such that S and P are each on a circle of diameter r, the radius of curvature of the grating. This circle is the Rowland circle, and, as noted above, the slit and spectra lie on this circle while the grating is tangent to it at the end of a diameter formed by the normal to the grating surface.

Since the same fundamental equation, $n\lambda = d(\sin \alpha + \sin \beta)$, holds for both the plane and the concave gratings, the expressions already derived for the angular dispersion and resolving power of the plane grating will also hold for the concave grating.

A convenient expression for linear dispersion is obtained by putting x for the distance CP on the arc of the Rowland circle. Then

$$\beta = \frac{x}{r}; \quad \frac{d\beta}{d\lambda} = \frac{1}{r} \frac{dx}{d\lambda}$$

whence, from Equation (43)

$$\frac{dx}{d\lambda} = \frac{nr}{d \cos \beta} \qquad (51)$$

For $\beta = 0$, the linear dispersion is a constant and departs but slowly from its normal value for small values of β.

50. The Astigmatism of the Concave Grating

The concave grating, by virtue of the fact that it is ruled on a concave mirror, introduces in the spectral line image the defects of the concave mirror—chiefly astigmatism. The theory of the astigmatism of the concave grating was first developed by C. R. Runge.[10] As a result of this astigmatism, a point on the slit is imaged as a line whose length, z, is obtained by multiplying the length of the ruled lines on the grating by a factor, k, such that

$$z = (\sin^2 \beta + \sin \alpha \tan \alpha \cos \beta)l = kl \qquad (52)$$

[10] Runge and Mannkopf, *Zeits. f. Physik*, **45**, 13, 1927; Dieke, *J. Opt. Soc. Am.*, **23**, 274, 1933, or Meyer, "*Diffraction . . .*," p. 435.

It is obvious that k increases rapidly with α and may be greater than unity for large values of α.

The values of k for all angles of incidence and diffraction are given in Figure 52. The solid curves connect points for which k has the constant value given beside the curve. For any pair of values of α and β, the value of k may be read from the curve and gives the factor by which the length of grating ruling must be multiplied to give the length of the image of a point on the slit. The dashed curves show, for a number of
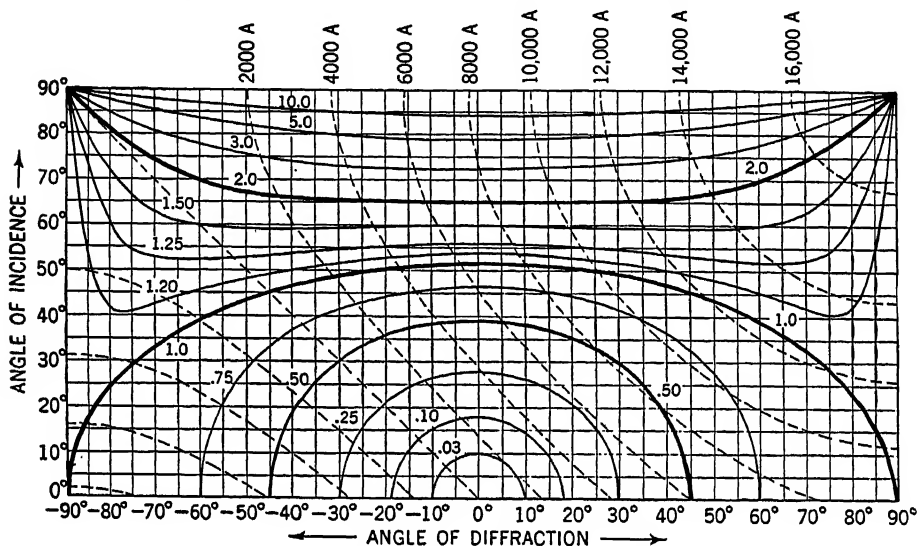
Fig. 52. The Astigmatism of the Concave Grating. The image length of a point source on the slit is given in units of the length of the rulings. The dashed curves give wave lengths at any angles for a 30,000-line grating.

wave lengths, the possible values of α and β for the first order of a 30,000-line-per-inch grating.

As a result of astigmatism, the spectral line formed by a grating is made up of a series of overlapping astigmatic line images. As a consequence, it is necessary that the slit be closely parallel to the rulings on the grating so that these astigmatic line images may fall on one another to produce sharp spectral lines. Furthermore, to obtain the maximum intensity of line, a large number of these astigmatic images of slit points should coincide; that is, a long length of slit should be illuminated. In fact, the brightness of the image will increase with slit length until the slit length is

$$l \left\{ \frac{\sin^2 \beta \, \cos \alpha}{\cos \beta} + \sin^2 \alpha \right\} \tag{53}$$

In contrast, it should be recalled that for stigmatic spectrographs, the intensity of the line image does not depend on the slit length.

The astigmatism makes it impossible to photograph, for comparison, two spectra in juxtaposition by illuminating one portion of the slit with one light source and an adjacent portion with another, as is customarily done with stigmatic instruments. One simple way to obtain sharply separated, adjacent spectra is to use, in front of the photographic plate, a movable shutter which exposes different strips of the plate to the different spectra. Spectra may also be differentiated by the aid of a
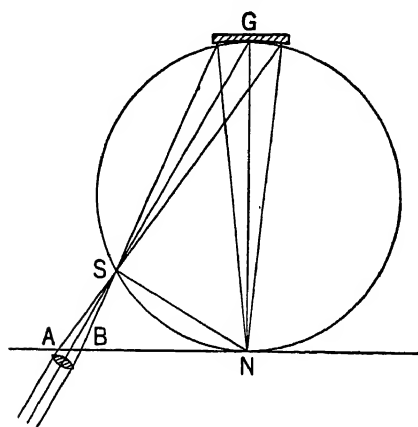
Fig. 53. Sirk's Construction for the Horizontal Image Line of a Concave Grating.

geometrical relationship pointed out by Sirks.[11] Sirks observed that, while vertical lines, such as a slit, at any point on the Rowland circle are imaged after diffraction at some point on the circle, horizontal lines must be farther from the grating than the Rowland circle if they are to be imaged on the circle. Thus, in Fig. 53, the grating G forms on the normal, at N, diffracted images of the vertical slit at S. Horizontal lines, AB, on the extension of the rays from G to S will be imaged also at N, if AB is on the tangent to the circle at N. A comparison prism or diaphragm placed at AB will be sharply imaged and may be used to separate the spectra from two sources.

51. The Wadsworth Arrangement of the Concave Grating

With one major exception, all the mountings of the concave grating are based on the Rowland circle arrangement; the exception is the mounting of the grating in parallel light devised by Wadsworth.[12] In his original mounting, Wadsworth used a collimating lens to render parallel the light entering the spectrograph. The more modern adaptations use a concave mirror for this purpose both for compactness and to avoid the use of transparent media. The slit is placed beside the grating, while the concave mirror is then at the opposite or plate-holder end of the mount (Fig. 54).

The diffracted rays are focused to form a spectrum on a curve, the equation of which is easily obtained from Equation (49). Since the source is at infinity, for a parallel beam, $s = \infty$; and since the spectrum

[11] Sirks, *Astronomy and Astrophysics*, **13**, 763, 1894.

[12] F. L. O. Wadsworth, *Astrophys. J.*, **3**, 54, 1896; W. F. Meggers and K. Burns, *Bur. of Stand. Sci. Papers*, **18**, 185, 1922.

is observed at or close to the grating normal, cos $\beta = 1$. Making these substitutions, there follows at once,[13]

$$p = \frac{r}{\cos \alpha + 1} \qquad (54)$$

This equation is that of a parabola, which, of course, varies in curvature from point to point, so that a plate holder of adjustable curvature is necessary. In common use α will range from near zero to about 45°, with p varying consequently from about $.5r$ to $.6r$. Since the diameter of the Rowland circle is r, it is seen that the Wadsworth mounting is approximately half as large for a given grating as the Rowland circle mountings. The dispersion is correspondingly reduced in the ratio of the respective grating–plate distances, although the resolving power is unchanged.

Fig. 54. The Wadsworth Mounting of the Concave Grating. S, entrance slit; G, concave grating; M, concave mirror; P, plate holder; AB, rail for plate holder.

A major advantage of the mounting is that astigmatism vanishes on the grating normal and is practically zero over the whole usable spectrum, as is also the case for the second-order image errors of coma and spherical aberration. This perfection of the image, and particularly the lack of astigmatism, leads to a gain in image intensity from the greater concentration of the light. Also, since the grating is used at about half the image-distance, or four times the solid angle, the spectrum is made correspondingly brighter by this factor than the spectrum of the same grating in the Rowland circle mountings. This gain in illumination is to some extent vitiated by the loss in the reflection at the collimating mirror.

52. The Dispersion of Grating Spectrographs

Since the dispersion in any grating spectrogram follows the general law of diffraction for the grating, the various types of grating spectrographs may be treated in a general way.

A. *Angular Dispersion*. The expression for the angular dispersion of a grating (α constant), which was derived on page 123, is

$$\frac{d\beta}{d\lambda} = \frac{n}{d \cos \beta} \qquad (43)$$

---

[13] If β is not 90°, the expression is

$$p = \frac{r \cos^2 \beta}{\cos \alpha + \cos \beta}. \qquad (54A)$$

From this expression it can be seen that for a particular angle β, the dispersion is inversely proportional to the spacing of the rulings of the grating and directly proportional to the order, and also that the dispersion is independent of the angle α.   Gratings with different spacings or different orders for the same grating can be compared at the same angle β by the application of the above expression.   If different orders of the same spectral region are to be compared, the factor $1/\cos \beta$ is introduced; the dispersion in the second order may be greater or less than twice that in the first order according as β for the second order of a certain wave length λ_c is greater or less than β for its first order.   This
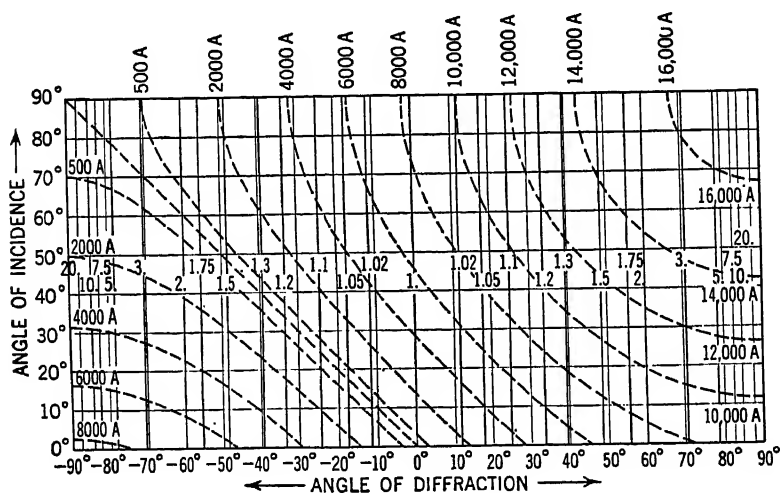
Fig. 55.   Dispersion of the Concave Grating in Terms of the Dispersion on the Normal.   Dashed curves give wave lengths at any angles for a 30,000-lines-per-inch grating.

relation holds also for the ratios of the dispersions in higher orders. Since for any wave length λ_c the value of β depends on α, the dependence of $d\beta/d\lambda_c$ on α must be considered, especially if a value of α is desired which will yield the highest possible dispersion for a given λ_c.

The diagram in Fig. 55 represents the angular dispersion of gratings; the values printed on the vertical lines are the factors for the various angles β if the dispersion $d\beta/d\lambda$ at the normal is taken as unity.

The angle of incidence for maximum dispersion at any λ_c can be readily calculated.   Since $d\beta/d\lambda$ is dependent on β, as expressed in Equation (43), the function $(d\beta/d\lambda)/d\beta$ must be investigated for its maximum values.   Differentiation yields the following expression:

$$\frac{(d\beta/d\lambda)}{d\beta} = \frac{n}{d} \frac{(-1)(-\sin \beta)}{\cos^2 \beta} = \frac{n}{d} \sec \beta \tan \beta \qquad (43A)$$

(Minimum dispersion is, of course, obtained for $\beta = 0$ when the spectrum is formed on the normal, as is the case for Rowland's and Abney's mountings. The corresponding angle of α is determined by $\sin \alpha = \lambda \, n/d$.) The value of β which yields a maximum dispersion may have a positive or negative sign with respect to that of α. In the function $n\lambda = d(\sin \alpha + \sin \beta)$, for positive β, both β and the expression (43A) will have a maximum value if $\alpha = 0$ for all wave lengths up to $n\lambda_c = d \sin \beta$. The maximum possible value is $n\lambda_c = d$, since β is then 90°. For larger values of $n\lambda_c$, maximum dispersion is realized for β near 90° and for values of α somewhat larger than are defined by $\sin \alpha > (n\lambda_c/d) = 1$. In the function $n\lambda = d(\sin \alpha - \sin \beta)$ for negative β, however, two different cases must be distinguished, of which only one applies to the customary use of the grating—when the spectra are photographed in the region between the slit and its direct reflection. The order of diffraction, n, will be defined as positive in this case. (The use of grazing incidence in vacuum spectrographs is an example.) In this range, $-\beta$ will be a maximum for the largest possible values of $\sin \alpha$—that is, for α approaching 90°. Accordingly, the two ranges mentioned yield opposite conditions for the choice of α, as small or as large as possible, respectively. The two ranges overlap for $\pm\beta = 30°$, $\sin \beta = \pm 0.5$, since then ($\sin \alpha + \sin \beta$) will have the value $+0.5$, for $\alpha = 0°$, $\sin \alpha = 0$, or for $\alpha = 90°$, $\sin \alpha = 1.0$, respectively. The wave length corresponding to these angular values is determined by $n\lambda_c = d/2$. As can easily be seen, the maximum dispersion for the case $0 < n\lambda_c < d/2$ will be obtained with α near 90°, and that for $d/2 < n\lambda_c < d$ with the choice of α near 0°.

Finally, the case of negative orders must be considered, as expressed by the formula: $\lambda(-n) = d(\sin \alpha - \sin \beta)$; λ, d, and α are, of course, always defined as positive quantities. The value of the function (43A) can now be made a maximum by choosing $-\beta$ near 90°, thereby determining a maximum value of α suitable for any λ_c from $\sin \alpha < 1 - \lambda_c n/d$

THE VALUES OF α AND β FOR MAXIMUM ANGULAR DISPERSION FOR THE VARIOUS WAVE-LENGTH RANGES (AND ORDERS) $n\lambda_c$

$n\lambda_c$	n		β	α
$0 < n\lambda_c < \dfrac{d}{2}$	$+$	$-$	$\sin \beta < \dfrac{n\lambda_c}{d} - 1$	$\approx 90°$
$\dfrac{d}{2} < n\lambda_c < d$	$+$	$+$	$\sin \beta < \dfrac{n\lambda_c}{d}$	$0°$
$d < n\lambda_c < 2d$	$+$	$+$	$\beta \approx 90°$	$\sin \alpha > \dfrac{n\lambda_c}{d} - 1$
$0 < n\lambda_c < d$	$-$	$-$	$\beta \approx -90°$	$\sin \alpha < 1 - \dfrac{n\lambda_c}{d}$

in the range $0 < n\lambda_c < d$. The results are represented in the table on page 133.

The maxima of angular dispersion given above have various values; the highest values possible are those occurring for $\beta \approx \pm 90°$. But there are other considerations, such as coma and intensity, which may reduce the utility of these regions of high dispersion. The region of negative orders has not yet been utilized in any mounting. The linear dispersion of the spectrum obtainable on the focal curve is, of course, fixed by the angular dispersion.
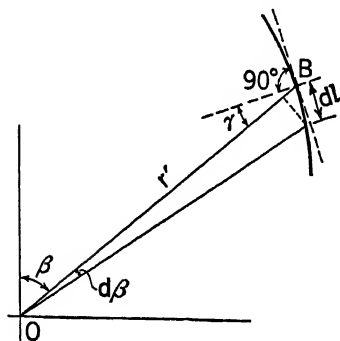
B. *Linear Dispersion; General.* The linear dispersion, $d\lambda/dl$, along the focal curve can easily be calculated by introducing into the formula (43) the dependence of dl at the focal curve upon the angle $d\beta$. The emergent light beam may strike the focal curve at any angle (Fig. 56) and at a distance r' from the center of the grating. The angle $d\beta$ is projected on the focal curve as a length dl, as follows:

Fig. 56. Relation between Linear and Angular Dispersion.

$$dl = d\beta \, \frac{r'}{\cos \gamma} \qquad (55)$$

By combining Equations (43) and (55), the formula for the linear dispersion is obtained:

$$\frac{dl}{d\lambda} = \frac{nr'}{d \cos \beta \cos \gamma} \qquad (56)$$

For the special applications of the grating, such as a plane grating with lenses, or a concave grating used on the Rowland circle or in a Wadsworth mounting, different expressions hold for the functional relationship between r' and $\cos \gamma$ and $\cos \beta$. By introducing the appropriate expression, one can evaluate the formula (56).

The expression "linear dispersion" is sometimes misused in the literature. Some authors use it to denote the constant dispersion maintained in the region about the normal of a concave grating, confusing the linear dependence of wave length upon distance at the plate with the conception of dispersion. As defined in this book, angular and linear dispersion may each be a constant or a function for a particular range.

The reciprocal value of the linear dispersion is often referred to in books and papers, and instead of $dl/d\lambda$, the value $d\lambda/dl$ is given in angstroms per millimeter, and this value is called the "dispersion." The less this number of angstroms per millimeter is, the greater is the real dispersion.

C. *Linear Dispersion of the Plane Grating with Lenses.* The formula (56) can easily be applied to the spectrum from a plane grating. The grating may be illuminated by parallel light; after diffraction, the light falls upon a lens that is chromatically corrected and aplanatic, so that the foci for the different wave lengths lie in a plane.

β (Fig. 57) is the angle subtended between the axis of the lens and the parallel rays of wave length λ_β coming from the plane grating; the angle $\beta + d\beta$ corresponds to the wave lengths $\lambda_{\beta+d\beta}$. The angle of incidence γ at the plate is then equal to the angle β; the distance of the image from
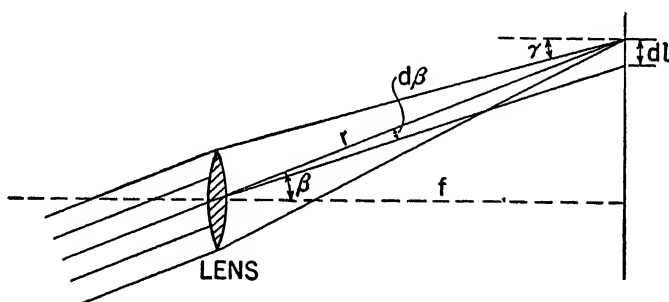
Fig. 57. Relation between Linear and Angular Dispersion with a Camera Lens.

the lens on its axis is its focal length f; for images off the axis, r' will have the value $r' = f/\cos \beta$.

The equation for these relations is as follows:

$$dl = d\beta \frac{r'}{\cos \gamma} = d\beta \frac{r'}{\cos \beta} = f d\beta \qquad (57)$$

The dependence of $d\lambda$ on $d\beta$ is given by Equation (43); the substitution into Equation (57) yields:

$$\frac{dl}{d\lambda} = f \frac{n}{d \cos \beta} \qquad (58)$$

The dispersion is seen to be proportional to the focal length f of the camera lens; for the dependence on n, d, β, and, indirectly, α, the same reasoning holds that has been given above for the angular dispersion.

D. *Dispersion of the Spectrum on the Rowland Circle.* The general formula can also be readily evaluated for the concave grating. Since the focal curve is a circle, the angle γ is determined by β (see Fig. 58), because, in the equilateral triangle OM_RB, the two angles β and γ are equal; M_R is the center of the Rowland circle. Furthermore, $OB = r' = r \cos \beta$. Therefore, from Equation (56) the expression for the dispersion is:

$$\frac{dl}{d\lambda} = \frac{nr}{d \cos \beta} \qquad (59)$$

This formula indicates that the dispersion is dependent on the angle β. Any wave length imaged at an angle β by a certain grating with particular values of d and r will have a dispersion that is a simple multiple of the order m.   The dispersion increases rapidly as grazing emergence ($\beta \to 90°$) is approached.   The function (57) is represented graphically in Fig. 55; the values given as parameters are in units of nr/d, making the minimum dispersion at the normal equal to unity.   The fact that the increase occurs slowly and independently of α induced Rowland and, later, Abney to use only the region around the normal of the concave grating for photographs. The deviation from the constancy in the dispersion for small values of β can be calculated by using the series development $\cos \beta = 1 - (\beta^2/2) + (\beta^4/24) - \cdots$.   When the first two members only are considered, a quadratic formula results which is a good approximation near the normal:
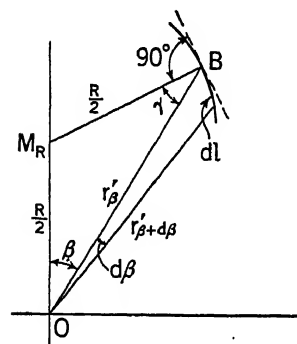
Fig. 58. Relation between Linear and Angular Dispersion on the Rowland Circle.

$$\frac{dl}{d\lambda} = \frac{nr}{d}\left(1 + \frac{1}{2r^2}\right) \qquad (60)$$

The numerical evaluation shows that for $\beta = \pm 5°$, the value of $dl/d\lambda$ is 0.38 per cent, and for $\beta = \pm 10°$, 1.52 per cent greater than its minimum value at the normal.

The numerical values for the dispersion on the normal to the grating are given in the following table.

RECIPROCAL DISPERSION $d\lambda/dl = d\cos\beta/rn$ ON THE NORMAL FOR THE ROWLAND MOUNTING (in A per mm)

d	$r =$ 30 ft.	21 ft.	12 ft.	1.00 m
$\dfrac{15{,}000 \text{ lines}}{2.5 \text{ cm.}}$	1.85	2.64	4.63	16.6
$\dfrac{30{,}000 \text{ lines}}{2.5 \text{ cm.}}$	3.71	5.29	9.27	33.2

Following the most common usage, it is not the values of the true dispersion $dl/d\lambda$ which are given, but their reciprocals, that is, the values $d\lambda/dl$ in A per mm on the plate (see page 134).

For the use of the concave grating with large angles of α and β, that is, for grazing incidence in the vacuum ultraviolet, another approximate expression for the value of the dispersion may be used. Corresponding to the case on the normal, where the length l was measured

from the normal, the direct image, with $\beta = \alpha$, may be used as the zero point for the length l on the plate. Any wave length λ appearing on the plate is then defined by l and by an angle β. This angle β is the sum of α plus the angle of diffraction δ; therefore, $\beta = \alpha + \delta$. On the other hand, δ can be expressed by the arc l and the diameter of the Rowland circle as $\delta = l/r$; therefore, $\beta = \alpha + l/r$. The introduction of this value into Equation (59) yields the formula:

$$\frac{dl}{d\lambda} = \frac{nr}{d \cos [\alpha + (l/r)]} \qquad (61)$$

for grazing incidence.

In the various ranges of α and l, various methods of approximation will be appropriate for the evaluation of this formula. The general result is that the dispersion for the range of very short wave lengths (l constant) is dependent upon the angle α; as α approaches 90°, the dispersion increases rapidly. This behavior can be seen on the diagram of Fig. 55. The apparent contradiction between the earlier statement, derived from Equation (59), that the dispersion is independent of α, and the formula (61) is explained by the change in the variables. In the latter case, the constant factor is not a fixed range β on the circle, but rather a fixed range of short

Fig. 59. Relation between Linear and Angular Dispersion in the Wadsworth Mounting.

wave lengths λ, whose emergence at β_λ is itself dependent on α in an approximate linear relationship.

E. *The Dispersion of the Spectrum for a Grating in a Wadsworth Mounting.* The formula (56) is sufficiently general for calculating the dispersion on any focal curve of radius r'_β of a grating, if that curve is a function of r, α, β, and γ. But it is necessary to express the angle γ of the light beam striking the focal curve, as well as r'_β, as an explicit function of those quantities.

It is obvious, from Fig. 59, that the direction of a focal curve is dependent on the change of dr' in the range $d\beta$. The angle $d\beta$ is projected on the focal curve as $dl = r'd\beta/\cos \gamma$. The angle γ between r'_β and the normal to the curve appears in the small right triangle that is formed with dl as the hypotenuse and dr as one leg. Therefore:

$$\sin \gamma = \frac{-dr'}{dl} = \frac{-dr' \cos \gamma}{r'd\beta}$$

Hence:

$$\tan \gamma = \frac{-1}{r'_\beta} \frac{dr'}{d\beta} \tag{62}$$

This formula is quite general; it would have been possible to use it for deriving the focal curves in the preceding sections. One can obtain the condition for the Rowland circle by substituting $r' = r \cos \beta$:

$$\tan \gamma = \frac{-1}{r \cos \beta} r(-\sin \beta) = \tan \beta$$

Therefore, $\gamma = \beta$, which follows from the simple geometry of the circle. The general formula (62), however, is indispensable for calculating the dispersion on less symmetrical focal curves, as in the case of the Wadsworth mounting, for which the following formula for r' holds:

$$r' = r \frac{\cos^2 \beta}{\cos \alpha + \cos \beta} \tag{54A}$$

Substituting this expression into Equation (62) yields the formula for the angle γ:

$$\tan \gamma = \frac{-(\cos \alpha + \cos \beta)r[-2 \cos \beta \sin \beta(\cos \alpha + \cos \beta) + \cos^2 \beta \sin \beta]}{r \cos^2 \beta(\cos \alpha + \cos \beta)^2}$$

$$= \frac{\sin \beta \cos^2 \beta + 2 \cos \alpha \sin \beta \cos \beta}{\cos^2 \beta(\cos \alpha + \cos \beta)} = \frac{\sin \beta(\cos \beta + 2 \cos \alpha)}{\cos \beta(\cos \beta + \cos \alpha)}$$

$$\tan \gamma = \tan \beta \left(1 + \frac{\cos \alpha}{\cos \alpha + \cos \beta}\right) \tag{63}$$

The angle between the light beam and the normal to the focal curve is dependent on both α and β. For grazing incidence, $\alpha \to 90°$, the value of $\cos \alpha$ will approach zero and γ will become equal to β, in agreement with the earlier result given above for the focal curve. The focal curve is a lemniscate which will change its shape to approach a circle for $\alpha \to 90°$; it was shown that $\gamma = \beta$ holds for the circle.

For the boundary condition $\alpha \to 0°$, Equation (63) becomes:

$$\tan \gamma = \tan \beta \left(1 + \frac{1}{1 + \cos \beta}\right) = \tan \beta \left(1 + \frac{1}{2 \cos^2 (\beta/2)}\right)$$

The large fraction in the parenthesis approaches the value $\frac{1}{2}$ for the region of the normal. Therefore, for short wave lengths (α and β small), the limiting expression will assume the value:

$$\tan \gamma = \tfrac{3}{2}(\tan \beta)$$

This formula describes the curvature at the vertex of the lemniscate which has the largest eccentricity of all the focal curves for the various

values of α. With increasing α, the factor $\frac{3}{2}$ decreases to unity for $\alpha = 90°$.

With the introduction of these new concepts, the general formula (52) can be applied to the Wadsworth mounting; it is only necessary to introduce r' and $\cos\gamma$ as explicit functions of r, α, and β. The formula (63) must be transformed by introducing for $\cos\gamma$ the expression:

$$\cos\gamma = \frac{1}{\sqrt{1 + \tan^2\gamma}} = \frac{1}{\sqrt{1 + \tan^2\beta\left(1 + \dfrac{\cos\alpha}{\cos\alpha + \cos\beta}\right)^2}}$$

$$\cos\gamma = \frac{\cos\alpha + \cos\beta}{\sqrt{(\cos\alpha + \cos\beta)^2 + \left[\dfrac{\sin\beta}{\cos\beta}(2\cos\alpha + \cos\beta)^2\right]}}$$

$$\cos\gamma = \frac{\cos\alpha + \cos\beta}{\sqrt{(\cos\alpha + \cos\beta)^2 + (\sin\beta + 2\cos\alpha\tan\beta)^2}} \tag{64}$$

The denominator of this expression can be simplified, but it becomes thereby less convenient for numerical evaluation.

By introducing Equation (64) and r' [Equation (54A)] into Equation (57), the linear dispersion on the focal curve of the Wadsworth mounting can be expressed as follows:

$$\frac{dl}{d\lambda} = \frac{nr\cos^2\beta}{d\cos\beta\,(\cos\alpha + \cos\beta)\cos\gamma}$$

$$\frac{dl}{d\lambda} = \frac{nr\cos\beta\,\sqrt{(\cos\alpha + \cos\beta)^2 + (\sin\beta + 2\cos\alpha\tan\beta)^2}}{d\,(\cos\alpha + \cos\beta)^2} \tag{65}$$

Examination of this formula leads to the following relations: For any angle of incidence α, the dispersion of the focal curve has a minimum value for $\beta = 0$; there is, however, no "normal dispersion" (in the sense of Rowland) for this mounting, because the dispersion on the normal depends on the angle of incidence α. By setting $\beta = 0$, Equation (65) is greatly simplified and yields as a function for the dispersion at the normal:

$$\frac{dl}{d\lambda} = \frac{nr}{d\,(\cos\alpha + 1)} \tag{66}$$

For small angles of incidence (very short wave lengths), the value of the parenthesis in the denominator approaches 2; the dispersion has, therefore, half the value that the same grating would produce if mounted on a Rowland circle. For increasing α, the fraction increases. For 90° incidence, the dispersion at the normal will finally reach the value found on the Rowland circle [compare Equation (59)].

Since the large amount of spherical aberration that occurs for increasing β limits the useful range of the Wadsworth mounting to the neighbor-

hood of the normal, the question of the constancy of the dispersion in the region of small β is important. The substitution of the series development for β into Equation (65) is too cumbersome to be reproduced here. The result, however, is that the angular region of approximately constant dispersion is smaller than on the Rowland circle, and its extent depends on α. For small values of α, the same deviation from constancy is reached for the values of β only half as large; for large values of α, the conditions of the Rowland circle are approached.

Equation (65) has been evaluated, and the results are represented in the graph of Figure 60. It is apparent that, for small values of the
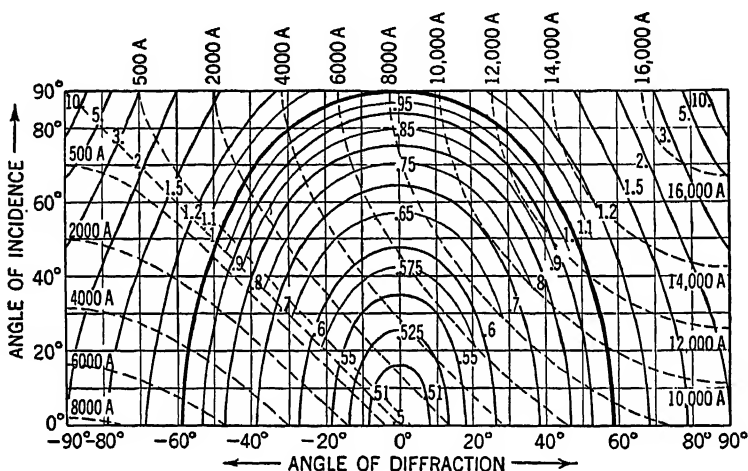
Fig. 60. **Dispersion of the Concave Grating in the Wadsworth Mounting in Units of** r/d. Dashed curves give wave length at any angle for a 30,000-lines-per-inch grating.

angle α, the minimum of dispersion is deeper and steeper than for large values.

53. The Production of Gratings

The ruling of optical gratings requires a high degree of skill in precision machining and frequent checking by very sensitive interference measurements, followed by corrections based on complicated mathematical analysis. Only a few laboratories in the world have been able to produce satisfactory results. Rowland's ruling engine, the most complete description of which has been given by H. Ames,[14] is still the prototype of all the machines that are in operation today. The more recent machines, however, embody a certain number of improvements.

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[14] H. Ames, in Rowland's *Physical Papers*. Baltimore: Johns Hopkins Press, 1902; also C. F. Meyer, *Diffraction* . . . , p. 128.

For most photographic applications, concave gratings have now replaced plane gratings, except for a few cases where extreme resolving power is desired. The principal application of plane gratings today is in the infrared, where they are used with concave mirrors and thermocouples.

Concave gratings are commonly ruled on mirrors (blanks) of radii of curvature of 1 meter, 2 meters, 10 feet, 21 feet, 30 feet, and 10 meters. However, since each concave mirror is ground and polished individually, there are usually slight variations from these lengths. The number of rulings per inch is usually approximately 15,000 or 30,000, although some gratings are made with 25,000 lines per inch, and, for infrared spectroscopy, much coarser gratings are used—even with only a few hundred lines per inch. On large gratings, the total number of lines on a grating reaches 200,000 or more, but often the imperfections in the ruling prevent the use of the whole area.

54. The Grating Blank

Material. Early optical gratings were ruled on speculum metal, an alloy of 33 per cent tin and 67 per cent copper, which was invented some two hundred years ago and is still used for some gratings. It is brittle and hard and can be polished to a perfect optical surface. In the visible region it has high reflectivity, but in the ultraviolet this property decreases rapidly and falls to about 25 per cent at 2000A. Another disadvantage of speculum metal is the fact that it tarnishes easily in air. Gratings can, however, be cleaned readily by methods that will be explained later.

Speculum metal as a material for gratings has been replaced to a large extent by aluminum, which has a higher reflectivity in the ultraviolet. Since a solid piece of aluminum cannot be polished easily to an optical surface, R. W. Wood used a blank of glass figured to the exact surface and coated it with an aluminum layer by evaporation. Thin aluminum layers sometimes have a tendency to peel off the glass; therefore, a layer of chromium is evaporated onto the glass to serve as cement for the evaporated aluminum layer. The grooves are ruled into this aluminum, probably penetrating into the chromium layer, and the ruling diamond stands up much better and shows less wear than when used directly on glass or even speculum metal.

Satisfactory as this method may be for the physicist performing the ruling, the experimenter who uses such a grating always faces the danger that some accident may cause acid vapors, chlorine, or mercury vapor to reach the grating and to destroy it. Such gratings should always be covered when not in use, because any damage to the aluminum layer destroys the grating itself.

Another method of obtaining a high reflectivity is the evaporation of aluminum onto a grating ruled on speculum metal or on glass. The layer of aluminum must be of a uniform thickness; the variation must be much less than the distance between adjacent grooves—a result which can be achieved by controlling the conditions of evaporization. The procedure is very satisfactory even for the largest gratings, which have been ruled at the University of Chicago, with 30,000 lines per inch and eight inches of ruled surface. The aluminum changes neither the intensity distribution over the different orders nor the selective reflectivity for certain angles. If this aluminum layer tarnishes so much that simple cleaning becomes unsatisfactory, the layer can be removed by a 5 per cent solution of sodium hydroxide. After a thorough washing and cleaning of the grating, a new aluminum layer can be evaporated upon the surface, which will then show the original spectral distribution again.

Gratings made for use in the near infrared have sometimes been coated with gold in order to insure longer life of the reflecting surface. The coarser gratings for the far infrared are usually ruled on solder metal.[15]

From the viewpoint of the optical properties of the grating, glass is desirable as the material for the blank because of its smaller thermal expansion coefficient. Fused quartz is still better and may be the grating blank substance of the future, if it can be molded in sufficiently large pieces without bubbles, and if it can be satisfactorily polished to an optical surface and can be ruled directly. The use of glass necessitates a choice of one of two compromises: to risk the diamond by ruling directly on glass on the chance of obtaining a good grating that can be aluminized and realuminized dozens of times, or to cover the glass with chromium and aluminum and to rule on that metallic layer, leaving it to the experimenter to take extraordinary care to avoid the early destruction of his grating.

Glass itself has a satisfactory reflectivity for very short wave lengths below 1000A, because the reflectivities of metals become very poor also in that region. For very short wave lengths and for grazing incidence, glass is completely equivalent to the other substances as a reflector.

The perfection to which the plane or spherical surface of the blank must be figured and polished depends on the size and the intended purpose of the grating to be ruled. However, the surface must be good in any case. The image formation is damaged if any part of the ruled surface introduces in the diffracted wave front a phase difference of as much as $\lambda/2$ (that is, one-half of a fringe in any interference pattern) for the shortest wave lengths that are to be diffracted by the grating.

[15] H. M. Randall, *J. App. Phys.*, **10**, 768, 1939.

If it is proposed to make observations of 2500A in first order, then the blank must be exact within 2500A/2, about one-quarter of a fringe in green light. For a grating that is to have the theoretical resolving power for the second order of 2500A, the deviations in the blank cannot be larger than 2500A/4, or one-eighth of a fringe of green light. To have 2000A in the fifth order fully resolved requires, therefore, a blank that is exact to one-twenty-fifth of a fringe—and the same accuracy is necessary to get the first order of 200A with full resolving power. This accuracy can be obtained only by the most skillful optical mechanicians, using the most sensitive testing methods.

55. The Ruling of Gratings

Since Rowland's time, the ruling has always been performed by a diamond point, drawn along the surface under a suitable pressure. Other conditions being equal, the diamond will form deeper grooves when the weight acting upon the diamond is increased. The more grooves per inch, the lighter the ruling must be. Gratings that are to yield a high reflectivity in the far ultraviolet must be very lightly ruled, so that they diffract the visible light only very slightly; the spaces between the rulings, that is, the remaining polished surface, act as the periodically diffracting elements. These gratings are the most difficult ones to produce; they must be ruled with a very sharp diamond point, which is likely to wear out or to break off much sooner than a more substantial diamond.

The diamond must move in a well-defined plane; it rotates about an axis fastened to a carriage which moves periodically in a very exact, straight line. At right angles to this line of motion a screw, the accuracy of which has been tested by interference methods, moves the blank between the successive strokes of the diamond. The movement, which is governed by precise gears, is adjustable, and its amount is the measure of the grating constant of the specific grating. The mathematical expression for the grating is satisfied by this arrangement: the grooves are ruled on the concave mirror so that they are equidistant along the chord.

56. Replica Gratings

Excellent replica gratings are now commercially obtainable that are copies from metal or glass gratings. They are made as collodion casts of the grating surfaces, mounted, after removal, on a silvered or transparent base of glass, which may be flat or concave.

The earliest successful replica casts were probably those made in England by T. Thorp, who obtained a British patent on his process (British patent No. 11466 (1899)). The method was later developed

by R. J. Wallace,[16] who is responsible for most of the present-day replicas. Professor R. W. Wood, of Johns Hopkins University, has also developed the replica technique. Some replicas are available which have been made under his supervision from master gratings ruled so as to concentrate 40 per cent of the diffracted light in the first-order spectrum on one side of the normal.

Plane and concave replica gratings are available in transmission and reflection types and in sizes up to four inches or more of ruled surface. They sell for ten per cent or less of the cost of original gratings. The best of them have a resolving power which is not greatly inferior to that of the original from which they were made. They are suitable for a wide range of instructional purposes and for the less exacting experimental applications. For spectrochemical and spectrophotometric work, there is reason to believe that they will, because of lower cost and readier availability, find an increasingly wide use. However, for research purposes and for other purposes where high resolving power or large aperture is needed, original gratings will continue to be preferred.

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[16] R. J. Wallace, *Astrophys. J.*, **22**, 123, 1905.

CHAPTER 7
The Diffraction Grating: Mountings and Use

57. Concave Grating Mountings

As already mentioned, all the mountings of the concave grating, except that of Wadsworth, are adaptations of the principle originally stated by Rowland, that the source and the diffracted spectrum lie on a circle to which the grating is tangent and which has as its diameter the radius of curvature of the grating blank. Various mechanical applications of the principle have been devised by different investigators. Several of these mountings are known by different names and have specific advantages and particular characteristics. Only the one originally used by Rowland is known by the name of the "Rowland" mounting, and this mounting, while once very popular, is at present less commonly used in new instruments than are some of the other forms.

58. The Paschen-Runge Mounting

Perhaps the most popular mounting at the present time for large gratings is that devised by Paschen and Runge.[1] In this arrangement (Fig. 61), a fixed slit or slits are set to give an angle of incidence determined by the problems to be handled. At the University of Michigan, one slit is placed near the normal for use in photographing first- and second-order spectra, while a second slit, at about 20° incidence, makes available the high dispersions of the fourth and fifth orders.

Fig. 61. The Paschen-Runge Mounting of the Concave Grating. *Sl*, slit; *G*, grating; *S*, light source.

The spectra from the slit or slits are focused along the Rowland circle, *PP'*, and the particular feature of this mounting is that arrangements are made for placing photographic plates along a large part of this circle and thus for photographing simultaneously a much wider spectral range than is possible with any other mounting. Only that

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[1] C. R. Runge and F. Paschen, *Abhand. d. K. Akad. d. Wiss. z. Berlin*, Anhang, 1, 1902.

region which falls at or near the grating normal will have a "normal" dispersion, but the disadvantage of nonlinear dispersion is, for many applications, far outweighed by the advantage of photographing a large part of the spectrum with one exposure.

The grating is usually mounted on a pier insulated against the vibration of the building. The photographic plates are clamped to rails bent according to the Rowland circle or, more precisely, to the focal curve of the individual grating used. This focal curve is determined, as shown above (page 128), by the radius of curvature of the blank, and is modified by the error of run (see Sec. 68) in the particular grating. The rails are likewise supported by piers insulated against vibration. The slit also should be rendered vibration-proof; it usually interrupts the track of the rails, since these are constructed to reach as near to the slit as possible because this region is optically very valuable, as the angles of incidence and diffraction are nearly equal. Probably the best way to protect the whole spectrograph against the vibrations of the building is to mount all the piers that support slit, rails, and grating on one heavy block of concrete which forms the floor of the spectrograph room and is insulated from the building by a space of one-inch width filled with damping material. Any shift in the position of the concrete block as a whole does not affect the relative positions within the optical system. For most Paschen-Runge mountings, an angle of incidence of about 45° is chosen, since it makes accessible for photography the range of long waves or of high orders. A larger angle of incidence would be still more favorable in that respect; but the optical errors in the image-formation increase rather rapidly as the angles become large. Accordingly, the preservation of the maximum resolving power could be accomplished only by reducing the length of the slit and/or of the rulings of the grating, thus greatly decreasing the intensity. Of course, smaller angles of incidence may be chosen. The 30-foot University of Chicago mounting carries three gratings, for which the angles of incidence range from 13.5° to 20.2°.

The choice of the angle of incidence should be determined by the individual grating available. For a grating that shows only slight preference in its reflectivity for different angles, the choice of the angle of incidence is not critical at all. But for gratings with a definite angle of highest reflectivity, the spectral region and order for which it is to be used most frequently will determine the choice. There is, of course, the possibility of mounting two slits at different angles on the circle, but this arrangement does not permit the best results with both slits. Theoretically, by having one slit at about 20° and the other at about 50° on the same side of the normal, it is possible to cover a very wide range of wave lengths within the angles of preferred reflectivity of the grating. Difficulties arise if one wants to obtain the maximum resolving

power with each slit. A satisfactory resolution can be obtained only by having the grating mounted "in aberration" (see Sec. 65C) and only if the true Rowland circle has been retained as the focal curve of the grating. Then both slits may be placed on the Rowland circle, and only small slit displacements are needed to take care of the slight deviations which are to be expected in the two focal curves.

The name *Paschen circle* is also applied to those mountings in which the rails do not cover a large part of the Rowland circle, but only some
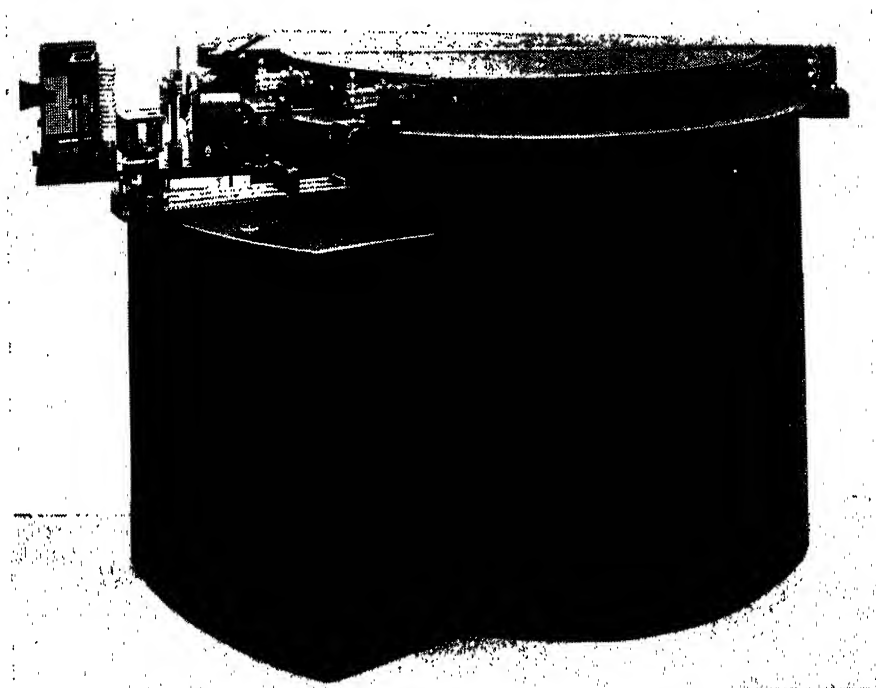
Fig. 62. Paschen-Runge Mounting of 150-cm Concave Grating. Shown with arc stand, condensing lens, and rotating sector before slit.

fraction of it, the criterion for a Paschen mounting being the fact that neither the plate holders, the grating, nor the slit is provided with any mechanical means for changing its position in order that different ranges of wave lengths or orders may be covered. Since the high reflectivities of gratings can be obtained only over very small ranges of angles of incidence, use of a multiple arrangement of gratings with this mounting is very effective, the respective angles of incidence being so chosen that adjacent spectral ranges are covered by the different gratings. This arrangement seems to offer the ideal solution for combining high resolution and strong intensity in one spectrograph arrangement.

At the Massachusetts Institute of Technology, three concave gratings with a radius of curvature of 35 feet are mounted in the same room. The slits are arranged close to each other.   An ingenious arrangement is applied for saving the light and using all three gratings simultaneously. The light is focused by a lens on the first slit, the jaws of which are plane and aluminized, thus reflecting the unused light back to another concave mirror which focuses the light on the second slit, whence the unused light is reflected in the same way to the third slit.   Thus, the same light source is used for the three gratings, and three spectra are photographed simultaneously, each being diffracted by that grating which has a maximum of reflectivity for the wave-length range it covers.

An example of a small Paschen mounting is the Applied Research Laboratories-Dietert spectrograph shown in Fig. 62.   This instrument has a 24,000-line-per-inch grating, of 150-cm radius of curvature, with a reciprocal dispersion of 7A per mm.   By removing two screws, it is possible to use the slit in either of two positions, for different spectral ranges.   At each setting, a region of about 2000A can be photographed on a 32-cm film.   A film spool carries 100 feet of film, and so a large number of exposures can be made rapidly.   As an exposed strip of film is drawn out of the end of the camera, a new piece is pulled into position.   The camera can be racked up and down to place as many as ten exposures on a single length of film.   The sector disc shown in the figure is placed at Sirk's horizontal focus (see Section 50).

All other grating mountings are characterized by a plate holder which is much smaller than that used in Paschen mountings, and which covers only a small range of wave lengths and orders, thus necessitating a change in position of slit, plate holder, or grating, or of two of these parts, to cover the whole wave-length range.   Some of these mountings have the advantage of requiring much less space than a Paschen mounting; others have optical advantages that may be valuable in special applications.

59. The Rowland Mounting

The oldest concave grating mounting, invented and constructed by Rowland himself, and described in 1883, satisfies in an ingenious manner the requirement that the slit, grating, and plate holder shall all be on the Rowland circle.   The grating and the plate holder are fastened on the opposite ends of a long, rigid bar so that the distance between the grating center and the middle point of the plate holder is equal to the radius of curvature (R) of the blank, while the plate holder has the curvature of the Rowland circle with a radius $R/2$.   Small carriages, free to rotate on axes below the center of the grating and below the center of the plate holder, and sliding on rigid rails, support the ends of the bar.   These two rails, carrying grating and plate-holder carriages, respectively,

intersect at an exact right angle, and above this intersection is placed the slit with its jaws perpendicular to the rail which carries the grating. From this description and Figure 63, it can easily be seen that the center of the grating, the slit, and the plate will be located on an exact circle, since the right angle whose sides go through the grating and plate-holder centers is always inscribed in the circle whose radius is the diameter of the Rowland circle.

The adjustment of the right angle, of the grating center, and of the slit above the center of the rail must be carried out with great care. The influence of small errors in the adjustment of the different parts of the mounting has been studied thoroughly by Kayser,[2] who gave the results of these calculations in extensive tables. Since this topic has been discussed thoroughly and the results are generally accessible, and since, furthermore, very few Rowland mountings have been constructed during recent years, they will not be treated here. At present it would hardly be justifiable to incur the trouble and expense necessary to construct a Rowland mounting of adequate precision and rigidity to use modern gratings of high resolving power. Other forms of mountings are usually preferred.

The optical properties of the Rowland mounting can be seen from Figure 55. The plates cover a range of about 10° or 15° on both sides of the normal to the grating, a range which exhibits a nearly constant and linear dispersion, showing only a slight increase in dispersion for increasing angles β and $-\beta$. This choice of small angles of diffraction was appropriate for the work that Rowland planned and executed. In his time, the grating was the best instrument available for exact measurement of wave lengths, and the linearity of dispersion was therefore very valuable. The Rowland mounting was rendered obsolete by changes in the character of spectroscopic problems. For one thing, with the development of interferometers, the more exact wave-length standards made possible the calculation of wave lengths in nonlinear spectra without loss in accuracy. The advantages, then, of other mountings, such as compactness in space, higher intensity, and the
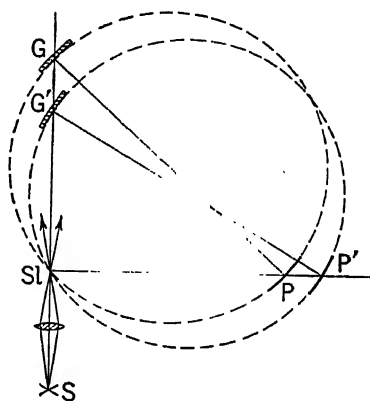
Fig. 63. The Rowland Mounting of the Concave Grating. The grating plate-holder bar which slides on the two perpendicular ways is shown in two positions, GP and G'P'. The slit, Sl, and source, S, remain fixed.

[2] H. Kayser, *Handbuch der Spectroscopie*, Vol. I, p. 470. Leipzig: S. Hirzel, 1900. E. C. C. Baly, *Spectroscopy*, Vol. I, pp. 183–194. London: Longmans, Green and Co., 1924.

accessibility in one setting of a larger range of wave lengths, led spec-
troscopists away from the use of the Rowland type.

It may be remarked that the dimensions of Rowland's original
apparatus constitute an excellent balancing of the various imperfections
in grating spectroscopy. He chose a radius of curvature of about
6 meters; his gratings had about 15,000 lines per inch and a ruled length
of about 6 inches. The linear diffraction width, determined by the
number of lines and the dispersion, yields a definition of the spectral
lines that is slightly smaller than the grain of the plates available at that
time, so that the theoretical resolving power of the grating cannot be
fully utilized, thus leaving some margin for imperfections in the ruling
of the grating. Of course, some imperfections in the mounting are
masked by the plate grain also; for instance, the parallelism of the slit
and the grooves of the grating cannot be maintained with extreme
precision when the bar is moved along the rails.

It will be seen by reference to Fig. 52 that the range of angles of
incidence and diffraction handled by the Rowland mounting is about the
least favorable with respect to astigmatism, thus unnecessarily increasing
the exposure times. The astigmatism vanishes for horizontal lines, and
they will be focused sharply on the plate if they are at the intersection
of the line from the grating to the slit and the tangent to the plate
holder at its center, as shown in Fig. 53. A step wedge can be placed
horizontally at this point, and its steps will be imaged sharply in reduced
size on the plate. This fact was pointed out first by Sirks.[3] Wadsworth[4]
constructed a mechanical arrangement to keep a diaphragm or a prism
for a comparison spectrum fixed at this point of intersection, no matter
how the plate holder is moved.

60. The Abney Mounting

Shortly after the publication of Rowland's arrangement, Abney[5]
devised another system for obtaining the necessary relationship between
the optical parts. He arranged grating and plate holder rigidly on the
ends of a heavy bar, as in the Rowland mounting. The bar, however,
does not move; it is kept fixed, and the slit moves on a radius bar about
an axis at the middle of the rigid bar. This principle is mechanically
sound because the movable part carries only the very light slit, and the
heavy grating and plate holder are firmly supported. Some incon-
venience arises because the jaws of the slit do not remain perpendicular
to the line from the slit to the grating as the slit is rotated around the
axis. It is therefore necessary to have the slit-holder rotate with the
slit itself as an axis. Furthermore, whenever the slit is moved for a

[3] J. L. Sirks, *Astronomy and Astrophysics*, **13**, 763, 1894.
[4] F. L. O. Wadsworth, *Astrophys. J.*, **3**, 47, 1896.
[5] W. deW. Abney, *Phil. Trans.*, **177**, II, 457, 1886.

change of wave-length range, the light source must be moved, and such movement may be quite inconvenient if heavy light sources and optical accessories are involved.

The optical properties of the Abney mounting are identical with those of the Rowland mounting, since here also the range covered by the plate holder is the part of the Rowland circle on both sides of the normal. The same properties of constant and linear dispersion and of very high astigmatism for large angles of α are inherent in the Abney spectrograph. The position for horizontal lines to be focused, as such, on the plates is the tangent to the plate holder at the normal, and mechanical means can be provided to have a step wedge or some optical instrument such as a prism for introducing a comparison spectrum sliding on this tangent as the slit is moved.[6]

Abney's mounting has probably never been constructed for gratings larger than a 3-meter radius of curvature. For modern gratings with 30,000 lines per inch and a total of 150,000 or more lines, the problem of keeping the slit parallel to the grating rulings with the accuracy necessary for utilizing the highest resolving power would present almost insurmountable difficulties.

61. The Eagle Mounting

A different type of grating mounting is that of Eagle,[7] which is similar in principle to the Littrow prism spectrograph, in that the slit and plate holder are mounted close together on one end of a rigid bar on the other end of which the concave grating is mounted. Again the plate holder covers only a part of the Rowland circle, about 20°–30°, but this part is no longer on the normal. The normal to the grating, therefore, makes an angle with the direction of the rigid bar (see Figure 64). As in the case of the Littrow mounting, it is necessary in the case of the Eagle mounting to rotate the grating around its vertical axis, and at the same time to move it along the rigid bar in order to adjust for different ranges of the spectrum; in addition, the plate holder must be rotated either around some axis in the plate surface or around the slit. It is therefore necessary to perform successively a number of different adjustments for each change of the wave-length range. These operations are quite time consuming, especially if a precise adjustment is desired.
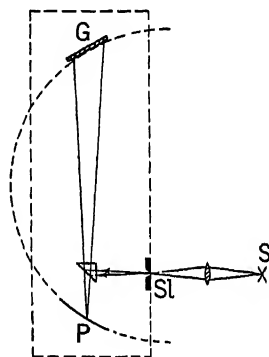
Fig. 64. The Eagle Mounting of the Concave Grating. S, light source; Sl, slit; G, grating; P, plate holder.

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[6] F. L. O. Wadsworth, *Astrophys. J.*, **3**, 47, 1896.
[7] A. Eagle, *Astrophys. J.*, **31**, 120, 1910.

In some commercial spectrographs, all these different motions are coupled together and governed by precise cams driven by an electric motor, while a scale shows the wave-length range covered by the setting at any instant. It is difficult to make such a mechanical system accurate enough to utilize the highest resolving power of modern gratings. The definition of spectral lines (imaged in a dispersion of 3A to 5A per mm) will, however, remain better than $\frac{1}{10}$ mm over the whole range of the spectrum. The angular range covered simultaneously in good definition may be as large as 30°.

The optical properties of the Eagle mounting are different from those of the mountings mentioned previously. In the diagram (Figure 55), the angular range covered by this mounting is located along the diagonal ($\alpha = \beta$) of the right-hand half of the figure. The dispersion on the plate is therefore variable, increasing toward larger wave lengths; furthermore, it changes from one setting to another, increasing toward longer wave lengths. The astigmatism is much smaller than for the same wave length in Rowland's or Abney's mounting. For short wave lengths, up to values of about 40° for the angles α and β, it is, in fact, near to the minimum values obtainable for these wave lengths by concave gratings. For larger angles, the astigmatism stays within usable limits. It is larger, however, than for a Paschen mounting with about a 40° angle of incidence. It may be emphasized that the longest wave lengths obtainable by any grating with a given number of lines are accessible only in an Eagle mounting or in a Paschen mounting with large angles of incidence, about 70° or 80°. A very large astigmatism is unavoidable in both cases.

The advantage of the Eagle mounting consists mainly in the fact that the arrangement is very compact. It is possible to mount a 6-meter grating in a space $1\frac{1}{2} \times 7$ meters—whereas other mountings require 7×7 meters—and to have the most useful parts of the spectrum, between the angles of incidence and diffraction of 10° to 45°, accessible for photography. On the other hand, the Eagle mounting has the disadvantage that extra precision is necessary in the mechanical parts. The grating must be mounted on a turntable which slides in accurate ways in the direction of the slit. The plate holder must be pivoted around the slit so that the slit is exactly on the axis of rotation.[8] If the grooves of the grating are perfectly parallel to the axis of the turntable and both are parallel to the slit and to the axis around which it is pivoted, then the adjustments for different ranges of wave lengths can be carried out in a relatively easy manner. Some trouble will always be introduced by the error of run inherent in the grating. The most

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[8] It is satisfactory if slit and plate holder rotate about any point of the Rowland circle. By proper compensation in the motion of the grating, the rotation of slit and plate holder about any vertical axis is permissible.

satisfactory way to correct for the deviation of the true focal curve from the theoretical Rowland circle is the method of mounting the grating in "aberration," which is treated in Section 65. The operation of "rolling" the grating, described in Section 65C, can be performed in a satisfactory manner by using an auxiliary point light source on the normal to the grating and rotating the grating through 180° around its normal. Another method of making the plate holder always fit the true focal curve is to have the curvature of the plate holder adjustable and to change the curvature slightly for the different settings of orders and wave lengths. If neither of these precautions is taken, it will not be possible to have all the lines in the whole range of the plate holder in the best definition, especially if the maximum resolving power is desired from the grating. If there is some reserve in resolving power, then for each wave-length setting an empirical set of data can be found which is sufficiently satisfactory.

The mechanical arrangement of the parts of the Eagle mounting differs in the various constructions; some of the variations will be considered from the viewpoint of their optical advantages, which are more important than their mechanical features. If the plate holder is pivoted not around the slit but around the center of gravity of the plate holder, then the angle of incidence will change slightly for different settings, with the resultant inconvenience of the necessity of changing the position of the light source. Furthermore, it will be much harder to maintain the parallelism of the slit if the slit is pivoted around an axis at a considerable distance.

The preferred side of the plate holder on which to place the slit depends on the size and purpose of the specific instrument. If the highest resolving power is desired, and some loss in intensity can be permitted, the coma must be kept within the limits of the diffraction width. For this requirement, the slit should be mounted at that side of the plate holder which is farther from the normal. However, if intensity is the main concern for the use of the specific instrument, the astigmatism should be kept within the smallest possible limit. The better position of the slit is then that nearer to the normal of the grating, since the astigmatism for long wave lengths is less if the angle of diffraction is smaller than the angle of incidence.

In some constructions the slit is mounted near the middle of the plate holder, but above or below it. Mechanically this solution is a convenient one, but optically it leads to serious difficulties. The coma of the spectral lines arising from this arrangement is large enough to destroy the line perfection. To place the slit and plate holder at different heights, and to have the Rowland plane halfway between their centers, is nearly equivalent optically to using a slit of the combined length of the slit, the spectral lines, and the space between. Since the coma and the curvature of the spectral lines are proportional to the square of the

distance of slit and spectral lines from the Rowland plane, their damaging effect will be perceptible for this arrangement, even for spectrographs of medium size and resolution. This slit arrangement is satisfactory in vacuum spectrographs only for the first order of very short wave lengths, say up to 1,000A, where the angles of incidence and diffraction are very small. It is, of course, necessary to keep the length of the slit and of the rulings short, and to have the plate holder directly above or below the slit, if this arrangement is to be used.

The large Eagle mounting for the concave grating made by the Baird Associates is shown in Fig. 65. The grating has 15,000 lines per
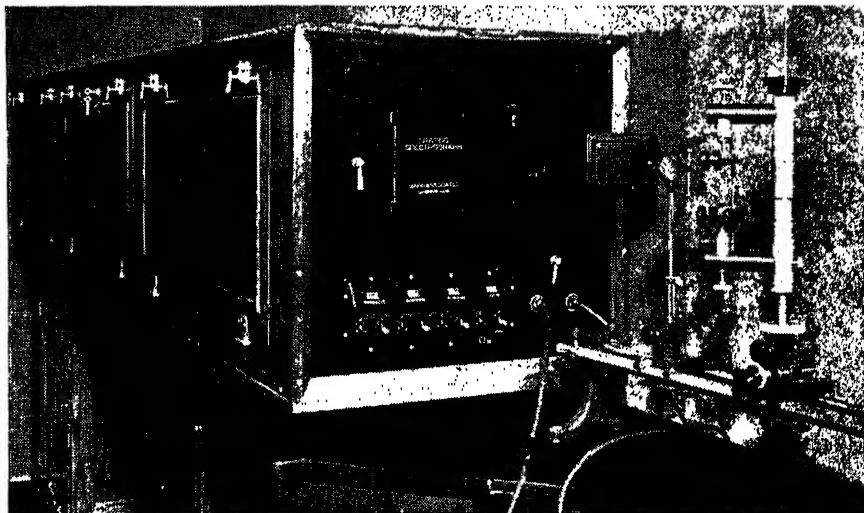
Courtesy of the Baird Associates.

Fig. 65. **Eagle Mounting of Three-Meter Concave Grating.** Arc stand and colli-
mating lens before slit.

inch and the inverse linear dispersion is about 5A per mm in the first order. A 4 × 10-inch plate covers about 1200A in the first order. All adjustments for different regions are made by small motors controlled by switches on the panel board under the plate-holder opening on the end of the housing. Veeder counters above the switches show the settings. Two-meter and one-meter instruments of similar design are also made by the same company.

62. The Radius Mounting

A new arrangement for mounting a grating spectrograph has been tried at the University of Chicago. This arrangement has decided advantages for vacuum spectrographs with nearly normal incidence, and is adaptable for large mountings constructed so as to cover the ultraviolet and the infrared regions.

The new mounting was designed to fulfill two conditions for a vacuum spectrograph: first, that the slit should be in a fixed position on the vacuum box, and second, that the plate holder should be fixed, small, and accessible through a separate opening in the wall of the spectrograph. The grating, however, does not have to be accessible from the exterior; inside the box it can take different positions on the Rowland circle, diffracting various portions of the spectrum to the plate holder. The grating holder is mounted at the end of a bar rotating about an axis, which is rigidly attached to the heavy bottom wall of the vacuum spectrograph and which constitutes the center of the Rowland circle. The grating holder slides on the bar in a plane perpendicular to the axis. It is then necessary to set the grating, the slit, and each point of the plate holder at the distance $r/2$ from the center of the axis. The plate holder is machined to a circle with radius exactly $r/2$.

For preliminary adjustment, a piece of tube carrying a pointer of the exact length $r/2$ can be mounted on the axis; with the help of this tube, grating, slit, and plate holder can be adjusted to within about .25 mm of their correct positions. For higher precision, the grating is turned until the slit lies on the grating normal. To make this adjustment, an auxiliary light source is placed before the lower half of the slit, and the image of the slit is reflected by the grating onto the upper half of the slit. With the help of a knife-edge test (see page 104), the slit can be adjusted to within .1 mm of the grating focus, especially if a point light source is used.

After the slit has been adjusted, the plate holder can be adjusted accurately in the same way. The grating is turned so that the direct reflection of the auxiliary light source at the narrow slit falls upon the plate holder. This reflection can be inspected by the knife-edge test, and the position of the plate holder can be corrected accordingly to within .1 mm. The grating can next be rotated on its radius bar in such a manner that the direct reflection falls successively upon different parts of the plate holder along its length, thus allowing the entire focal curve to be adjusted. An independent check of the adjustment can be made by turning the grating so that its normal intersects the plate holder, and by putting an auxiliary light source behind a small point opening placed in the plate holder near the normal. The direct reflection will then be imaged on the plate holder in a position symmetrical to the light source with respect to the normal, and a knife-edge test can be made. In general, this direct reflection will not lie precisely in the focal curve that was obtained by the use of a light source at the slit. The reason for this discrepancy is that the first knife-edge test determined the focal curve for the slit at the correct distance r from the grating, but not for the slit at the distance $r/2$ from the center of the Rowland circle. The center of rotation of the bar will in general not be the exact midpoint

of the distance between slit and grating. This small deviation, amounting ordinarily to not more than .5 mm, is not troublesome, since further adjustments must be made. The amount of the deviation and its sign should be measured, however, and be kept in mind for later purposes.

It was pointed out earlier that the presence of error of run in the grating changes the focal curve of the diffracted light from the focal curve for the direct image. The auxiliary light source at the slit is therefore replaced by a mercury lamp, and the grating turned so that visible spectral lines will be produced at the plate holder. By the knife-edge test, the deviation of the position of the image before or behind the plate holder is measured. The grating is then displaced to such a position that the spectrum on the other side of the normal will fall on the plate holder, and the position of a visible spectral line is again measured. The operation of moving the grating and radius bar can be replaced, if desired, by a rotation of the grating holder around the normal of the grating by 180°. In general, the images of the spectral lines for the two different positions will be displaced from the focal curve by equal amounts inside and outside of the focal curve. This deviation can be corrected for by "rolling" the grating around the Rowland circle, as is pointed out in Section 65C. The "rolling" operation also accomplishes, at the same time, a correction of the distance of the grating from the axis, a correction amounting to one-half of the discrepancy in the position of the direct image that was formed by a light source at the plate holder. The slit should, of course, be displaced in the same direction by the same amount. The amount of "rolling" necessary can be calculated approximately, and its effectiveness can be judged by the knife-edge test on the plate holder. Before the "rolling" has been carried out to a high precision, the plate holder should be readjusted, with the aid of the direct image, for the slight changes of slit and plate holder. Since the "rolling" must be carried out with high precision, a final check of the parallelism between slit and grating lines must be made. The "rolling" can be observed photographically by taking several pictures successively on the same plate. After the best position has been found, a correction can be made for the exact position of parallelism, using the split slit method. (See Section 66B.)

The advantage of the radius mounting is mainly that the knife-edge test can be used very extensively in its adjustment. The rotation of the grating along the Rowland circle moves the visible spectrum and the direct image across the plate holder, thereby allowing the use of the eye, instead of the photographic plate, for the adjustment. Even the range covered by the vacuum ultraviolet and by the ultraviolet in the final position of the grating can be controlled by the knife-edge test when the grating is rotated. The visual test can be carried through in a few seconds instead of the hours required for photographic tests with

extremely narrow slits; the time needed for a perfect adjustment is reduced from several weeks to several days, especially in the vacuum region. For the vacuum region there is another advantage: it is possible in the final adjustment to set the grating so that the direct image is just off the plate holder, thereby avoiding the overexposure and scattering that occur in the region around the direct image yet utilizing the advantage of adjusting the plate holder to the direct image.

The disadvantage of the radius mounting lies in the fact that the direction from the slit to the grating changes whenever the grating is moved. For the adjustment this is not very bothersome, but if the radius mounting is to be used in such a manner that different positions of the grating are utilized for obtaining different ranges of the spectrum on a plate holder of restricted length, then at every resetting of the grating, the light source must be moved. For large displacements of the grating, it will be necessary to turn the slit about its vertical axis. This rotation, of course, can be provided, but even if the mechanical parts are machined with high precision, the parallelism of the slit and the rulings may be disturbed. A possible compromise is to use the many settings only for the adjustment of the optical parts and to restrict the final use of the mounting to only two settings at the extreme positions of the grating.

In order to be able to reproduce the parallelism of the grooves and the slit in the two settings, it may be advisable to have the base plate of the grating holder adjustable by three set screws on the two horizontal fixed plates that define the two positions of the grating. If the base plate of the grating is leveled exactly by a spirit level, and the parallelism of the grooves is adjusted by the tangent screw of the grating, then for the other position of the grating the leveling of the ground plate will reproduce to a very high degree the parallelism of the grooves and the slit. The advantage in the case of a large grating is mainly that space can be saved. A 36-foot spectrograph does not require the use of a room 40 × 40 feet, but only about 22 × 40 feet, while the two different positions of the grating render the entire spectral range accessible.

63. The Wadsworth Mounting

The Wadsworth or stigmatic mounting illuminates the grating with parallel light, usually from a concave mirror (Fig. 54). Since in this case the slit can be placed beside the grating, the mounting is quite compact. Because of rapid increase of spherical aberration and astigmatism with angle of diffraction, the mount is usually arranged to work near the normal. The plate holder and grating are arranged at opposite ends of a bar which is pivoted about a vertical axis passing through the center of the grating. As the spectral region is changed, the arm slides along the ways AB. The distance from grating to plate holder, the tilt of the plate holder, and its curvature must all be altered for each new

setting.   The adjustment is therefore somewhat more complicated than in the Rowland circle mountings, which do not require the change of plate curvature.   For gratings of moderate size it is often possible to cover most of the useful range with one setting and so to avoid frequent adjustments.

The dispersion of the Wadsworth mounting is never truly normal, and the departure from linearity at any angle of incidence is more rapid than with the Rowland circle mountings (see Section 52).   The instrument, however, is usually not used for wave-length determination or in work in which linearity of dispersion is important.

The applications for the stigmatic mountings are chiefly those in which the stigmatic image formation makes it preferable to the Eagle mounting.   It has been used with the Fabry and Perot etalon for the
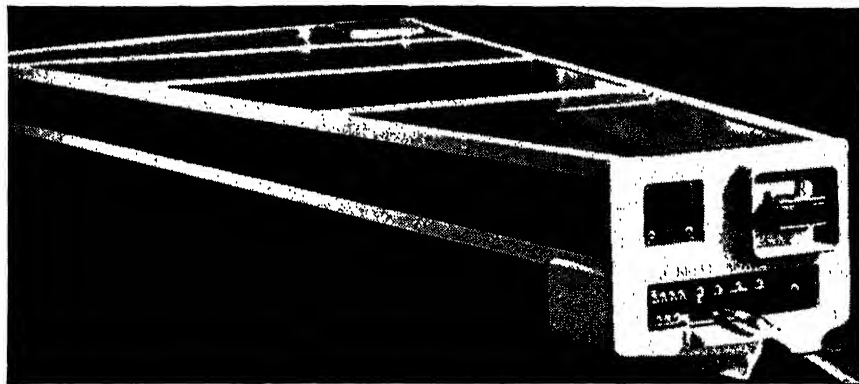
Courtesy of the Jarrell-Ash Company.

Fig. 66.   Wadsworth Mounting of a 21-Foot Concave Grating.   Optical bench before slit for mounting light source and accessories.

interferometric determination of wave length by Meggers and Burns, who have given a good description of the mounting and its use.[9]   It is also useful where a stigmatic slit image is needed, as in photometric work, with a stepped slit or sector.   For this reason it has been recommended and used for spectrochemical applications.[10]

A Wadsworth mounting manufactured by the Jarrell-Ash Company[11] is shown in Fig. 66.   A 15,000-line aluminum-on-glass grating of 21-foot radius of curvature gives an inverse linear dispersion of about 5A per mm. About 2500A in the first order are photographed on a 4 × 10-inch plate. An electric motor controlled from outside makes the adjustments for changing from one region to another, while a second motor racks the plate up or down.

[9] W. F. Meggers and K. Burns, *Bur. of Stand. Sci. Pap.*, No. 411.

[10] G. R. Harrison, *Proc. Fifth Summer Conference on Spectroscopy*, p. 31.   New York: J. Wiley and Sons, 1938.

[11] R. F. Jarrell, *J. Opt. Soc. Am.*, **32**, 666, 1942.

64. The Adjustment of the Concave Grating

In principle, the adjustments required in the focusing of a concave grating are few and simple. The grating must be leveled so that the normal to the center of the blank passes through the plane normal to the median line of the plate holder, and must be rotated until the grating lines are exactly normal to this plane. The slit must be centered accurately on this plane, located precisely on the Rowland circle determined by the grating radius, and rotated in its own plane until it is very accurately parallel to the grating rulings. The photographic plate must be fitted carefully to the Rowland circle and set normal to the plane of this circle. These adjustments are common to all "Rowland circle" mountings except a few small ones in which the slit is set above or below the plate holder. The grating normal then passes between them, while they are on great circles through the grating on the sphere which has the Rowland circle as an equator.

All grating mountings provide for certain movements of the grating, the slit, and the plate holder to permit these adjustments to be made initially, to allow for the compensation of certain grating errors in particular gratings, and to correct for temperature changes. To obtain the maximum resolving power of a large grating, great precision is required in adjustment. An understanding of the optical effects of small changes in the various motions of the grating and slit is necessary to carry out the focusing of the grating correctly and expeditiously. These effects will be discussed in some detail.

65. The Optics of Small Displacements of the Grating

The housing of the grating should fulfill two requirements: it must be very rigid, and it must permit displacements of the grating and also rotations around different axes, some of which may be restricted to small angles. The three mutually perpendicular axes through the center of the grating will be called the vertical axis L (along the length of the grooves), the horizontal axis W (in the direction of the width of the grating), and the axis normal to the blank, X.

A. *Rotation about the Horizontal Axis* W. It is evident that rotation around W raises or lowers the spectrum (and the direct image) with respect to the slit. The amount of the shift can be easily calculated by considering the relative position of slit and images with respect to the XW, or "equatorial," plane, which may be regarded as rigidly connected to the grating. If the grating is turned around the W-axis by the angle σ and the slit is kept fixed, then the mid points of all the images lie in a plane which makes the angle σ with the XW-plane, because they arise from a slit whose mid point lies in a plane at an angle on the other side of the equatorial XW-plane. The linear displacements of the spectral

lines arising from a rotation of the grating around the horizontal W-axis are the greatest at the normal, amounting to $2r \tan \sigma$, and they grow less for larger values of α and β. The displacement of the slit from the equatorial plane is $r \cos \alpha \tan \sigma$, and that of the line image is $r \cos \beta \tan \sigma$. The relative displacement of the images with respect to the slit is then

$$Z - Z' = r \tan \sigma \, (\cos \alpha + \cos \beta) \tag{67}$$

In any mounting such as the Rowland mounting, the Eagle mounting, or the radius mounting, this formula is useful for the adjustment of the grating and also for the calculation of the errors in the tracks in which the grating is being moved.

Both coma and curvature of the spectral lines are measured from the XW-plane. Both these faults damage the definition of the spectral line, and both increase with the square of the distance from the equatorial plane. It is desirable, therefore, that the slit and its image be located in the same plane. Mountings which place the slit above or below the plate holder will give an inferior definition.

B. *Rotation of the Grating about the Vertical Axis*, L. The rotation of the grating around the vertical axis through the center of the grating is an operation frequently carried out during the adjustment. This movement displaces the equatorial plane parallel to itself, but rotates the Rowland circle around the center of the grating. The image formation for a given λ or α is thereby affected in two distinct ways: the angles of incidence and diffraction are changed, and the position of a fixed slit with respect to the focal curve, or the Rowland circle, is changed. The latter effect is conveniently utilized in the adjustment. It must, in fact, be employed if one or more gratings are to be adjusted to a focal curve fixed in advance. Furthermore, the rotation about the vertical axis is an operation by which the effects on the focal curve of error of run (Section 68) can be partially compensated.

A rotation of the grating through the angle τ will change the angle of the direct image by 2τ, and the angle of diffraction of every spectral line will be changed by the same angle in the first approximation. A more accurate calculation can be carried out in the following way, calling χ the change in the angle of diffraction.

Before rotation:

$$\lambda = \frac{d}{n} (\sin \alpha + \sin \beta)$$

After rotation through the angle τ:

$$\lambda = \frac{d}{n} [\sin (\alpha + \tau) + \sin (\beta + \chi)]$$

$$\sin \alpha + \sin \beta = \sin (\alpha + \tau) + \sin (\beta + \chi)$$

$$\sin (\beta + \chi) = a = \sin \alpha - \sin (\alpha + \tau) + \sin \beta$$

$$= \sin \beta \cos \chi + \cos \beta \sin \chi \tag{68}$$

For small angles, χ is small and $\cos \chi$ can be assumed to be equal to 1. Then, with good approximation,

$$\sin \chi = \frac{\sin (\beta + \chi) - \sin \beta}{\cos \beta} = \frac{\sin \alpha - \sin (\alpha + \tau)}{\cos \beta}$$

$$= \frac{-2 \cos \left(\alpha + \frac{\tau}{2} \right) \sin \frac{\tau}{2}}{\cos \beta} \tag{69}$$

For larger rotations, the approximation $\cos \chi = 1$ does not hold. Substituting the value $\cos \chi = \sqrt{1 - \sin^2 \chi}$ in the expression $\sin \beta \cos \chi + \cos \beta \sin \chi$, there follows in such cases:

$$\sin \chi = a \cos \beta \pm \sin \beta \sqrt{1 - a^2} \tag{70}$$

Since a can be calculated, χ is simply determined. This equation is rigorous, even for grazing incidence, although at large values of the angles α and β, the error of run is not quite so disturbing as for medium angles.

It is also useful to calculate the shift of wave length, $\Delta\lambda$, which is caused at any given fixed point on the circle by the rotation τ. Since,

$$\lambda = \frac{d}{n} (\sin \alpha + \sin \beta) \text{ and } \lambda_\tau = \frac{d}{n} [\sin (\alpha + \tau) + \sin (\beta + \tau)]$$

where λ is the original wave length and λ_τ is the new wave length, by subtraction,

$$\Delta\lambda = \lambda_\tau - \lambda = \frac{d}{n} [(\sin \alpha + \sin \beta)(1 - \cos \tau) - \sin \tau (\cos \alpha + \cos \beta)]$$

$$= \frac{2d}{n} \left[\sin \frac{\tau}{2} \cos \left(\alpha + \frac{\tau}{2} \right) + \cos \left(\beta + \frac{\tau}{2} \right) \right] \tag{71}$$

For the wave length, which is imaged at the slit position, by setting $\alpha = \beta$, there follows:

$$\Delta\lambda = \frac{4d}{n} \sin \frac{\tau}{2} \cos \left(\alpha + \frac{\tau}{2} \right) \tag{72}$$

For small angles τ and α, the expression becomes:

$$\Delta\lambda = \frac{d}{n} 2\tau \tag{73}$$

which can be used with good approximation for larger angles.

Such small rotations of the grating about the direction of the spectral lines displace the focal curve, and they are therefore a necessary operation for the adjustment of the grating to a predetermined focal curve, which must be made with a large, rigid plate holder. The optical effect is as follows: the rotation of the grating about its vertical axis leaves the distance from the slit to the grating unchanged, but it displaces the focal curve. The distance from the slit to the grating is $r' = r \cos \alpha$, rather than $r'_r = r \cos (\alpha + \tau)$, which is the true value for its position on the new Rowland circle. Therefore, the distance of the slit from the new focal curve will be:

$$\Delta r' = r[\cos \alpha - \cos (\alpha + \tau)] = 2r \sin \frac{\tau}{2} \sin \left(\alpha + \frac{\tau}{2} \right) \qquad (74)$$

The locus for the spectral lines arising from this slit position off the focal curve can be calculated by introducing $r' = r \cos \alpha$ into the general focal Equation (49a), which holds for the new position of the slit. Then, writing α_r for $\alpha + \tau$,

$$\frac{\cos^2 \alpha_r}{r \cos \alpha} - \frac{\cos \alpha_r}{r} + \frac{\cos^2 \beta_r}{r'} - \frac{\cos \beta_r}{r} = 0 \qquad (75)$$

Hence:

$$r'_r = r \cos \beta_r \frac{\cos \beta_r}{\cos \beta_r + \cos \alpha_r \left(1 - \dfrac{\cos \alpha_r}{\cos \alpha} \right)} \qquad (76)$$

The new focal curve will lie nearer to the old one (for which $r' = r \cos \beta$) as the angle of rotation τ becomes smaller; the new curve will have no intersection with the old one. If τ is positive, $\cos \alpha_r < \cos \alpha$ and the focal curve will lie wholly inside of the Rowland circle. For negative values of τ, it is wholly outside the Rowland circle. For spectral lines near the slit (Eagle mounting), under the assumption $\alpha_r = \beta_r$, the change in the focal curve becomes

$$\Delta r' = r' - r'_r = r \cos \alpha_r - \frac{r \cos \alpha}{2 - \dfrac{\cos \alpha_r}{\cos \alpha}} = \frac{r \cos \alpha_r (\cos \alpha - \cos \alpha_r)}{2 \cos \alpha - \cos \alpha_r} \qquad (77)$$

As long as $\Delta r'$ is small, the aberration arising from the departure from the true Rowland circle can be shown to be insignificant. No perceptible loss in definition of the spectral lines on the new focal curve may result. Thus, the rotation of the grating around its vertical axis is one of the means of adjusting it for use with a given plate holder, since the radius of curvature of the focal curve can be slightly changed. The necessity for using this procedure arises from the fact that the plate holders are usually machined to have half the radius of curvature of the grating blank, while the actual focal curve deviates from the geometrical

Rowland circle considerably if the ruling of the grating contains an error of run. The adjustment of the grating includes, then, the operations to fit the machined circular curve to the actual optical focal curve.

C. *Rotation of the Grating about* X, *the Normal to the Blank.* The grating holder should provide for rotation of the blank around the normal in two different ways: first, by small amounts, in reproducible manner, and second, by a full 180°.

The latter rotation is useful in determining on which side of the grating normal the reflectivity of the grating is better for the wave length and order desired at any given angle of incidence. In the visible region, this determination may be made by inspection, but for the near or far ultraviolet, such determinations must be performed photographically. Since most gratings show ratios of two or more for their relative brightnesses on the two sides of the normal, the proper choice results in a large saving in the exposure time for each picture.

For both the ultraviolet and the visible regions, the rotation by 180° also serves the purpose of checking the grating for error of run. For any perfect grating, the rotation by 180° about the normal to the center of the grating gives an identical focal curve, that is, the true Rowland circle. The normal to the blank can easily be found from the fact that a small light source placed on the Rowland circle will, if on the grating normal, be imaged in itself. The grating should be adjusted in its holder so that a rotation of the holder by 180° does not move the normal. In this position, the holder should be clamped rigidly to its base, because only minor adjustments of the grating within its holder will thereafter be necessary and useful; the adjustment screws provided on the grating holder should permit such minor adjustments in a precise and reproducible way.

The importance of the rotation of the grating through 180° arises from the fact that the error of run of the grating rulings changes the focal curve for the grating spectra from the Rowland circle to an ellipse (in first approximation) the major axis of which is inclined to the normal. The spectral lines from a light source, for instance a mercury arc, mounted behind an auxiliary slit at the grating normal will lie outside of the Rowland circle on one side of the normal, but inside of it on the other. By the knife-edge test, the displacement can be easily measured; at about 30° from the normal, it amounts probably, for the best large gratings, to several inches.

This measurement of displacement can be performed only if a large part of the Rowland circle has been rigidly constructed, with the diameter r. If, as in most cases, only a fraction of the focal curve is built, the above-described test is not possible. It can be replaced by the rotation of the holder about its normal by 180°. By this means the two spectra, that on the right and that on the left of the normal to the grating, can be

imaged in turn at the same part of the focal curve. These two spectra should lie at equal distances inside and outside of the "rails" which carry the photographic plates.

The best procedure is not to adjust the rails, except to set them half-way between the two focal curves, but to rock the grating about its vertical L-axis in such a way that the point of contact of the grating with the Rowland circle "rolls" along the circle, so that a point on the grating, other than the center along the "equatorial line," will become tangent to the Rowland circle. By this operation the focus of the blank will be shifted, but will still remain on the Rowland circle—because the blank of the grating with the radius r forms a sphere, all points of which are equivalent. The direction of the "rolling" has to be chosen so that the spectral lines lying outside of the circle are turned toward larger values of β. If the light source with the auxiliary slit is kept fixed, its image will be shifted, but will still be found to be exactly on the Rowland circle. The rotation of the grating by 180° will then bring the image of the slit to the other side of the normal, but still on the Rowland circle.

By the operation of "rolling" the grating, the focal curves for the two sides of the grating are brought toward each other. Not merely then is the rotation of the holder a rotation of the grating around the optical normal; it also displaces the tangential point of the grating from one side of its geometrical center to the other. Consequently, the two direct images of the light source that were on the original normal now lie on different points of the Rowland circle. Therefore, the same wave lengths are found at different points of the circle for the two different positions of the grating, but the images are now displaced sideways to a much lesser degree than before, in front of and behind the focal plane. By measuring the amount by which the grating was "rolled" about the vertical axis, and by measuring the decrease of the displacement of the two spectra, it is possible to make a linear extrapolation and to adjust the "rolling" of the grating to the right amount.

It is not necessary to carry out this first "rolling" to an accuracy of better than a few millimeters. After it has been made, the rotation of the holder should be repeated, and this time the displacement of the two spectra with respect to the focal curve should be observed accurately. If the two spectra do not lie symmetrically inside and outside of the focal curve, then the slit should be moved until the symmetrical position is attained. Finally, the grating is rotated about L ("rolled") a little more until the spectrum which is the brighter one for the chosen position of the slit lies exactly on the focal curve.

These manipulations have the following advantages:

1. A larger part of the grating can be used; when the grating is "rolled" to one side, it is put into a position in which a perfect grating

would exhibit much "aberration." This imperfection in the image formation is used to compensate for the error of run in the ruling of the grating. The procedure will hereafter be called mounting the grating "in aberration."

2. A plate holder can be used that is shaped to a true circle, with the focal length of the grating as its diameter. A carefully machined circle will fit the exact focal curve over more than 90°.

3. This procedure allows the use of more than one grating with equal radii on the same circle, or of more than one slit for the same grating.

In connection with this rotation of 180° around the normal, if the limit of the resolving power of the grating is to be approached, a fine adjustment at each position is necessary in order to insure the exact parallelism of the slit to the rulings, that is, to the chords of which the rulings are the arcs. However, there should be a preliminary, approximate adjustment, to a fraction of a degree, before the "rolling" of the grating is begun.

A rotation of the grating about its normal leaves the focal point of the blank on the Rowland circle unchanged; furthermore, the position of all the direct images is unaffected, since the rulings do not take part in their formation. If, for simplification, it is assumed that a "point slit" is used, which may be located in the equatorial plane of the grating, the spectral lines have their mid points in a plane that is perpendicular to the grooves and that contains the directly reflected beam. A rotation of the grating around its normal by the angle σ will therefore rotate the plane containing the centers of the spectral lines by the same amount around the reflected beam.

With the help of two auxiliary light sources, this behavior can be used for adjusting the grating rulings, or better, their chords, to make them very nearly vertical in space. The procedure will be described in another section.

The requirement of exact parallelism of the rulings and the slit can best be met by a final adjustment of the slit, which can be made by means of a "tangent screw" in the mounting that allows a precise and reproducible rotation of the slit about the axis perpendicular to the slit and its jaws. In the rare case that the slit has already been precisely adjusted to another grating, the new grating itself must be brought into an accurate position. The optical effects of rotation of the slit will be discussed later. It should be noted, however, that, if the grating instead of the slit is rotated, an inversion in the direction of rotation of the spectral lines occurs, as well as a doubling of the angle of rotation.

D. *The Parallel Displacement of the Grating in the Direction of Normal to the Rowland Circle.* Since the exact focal curve of the particular grating is not known before it is mounted, provision for a displacement along its normal must be made. In the case of the Eagle mounting, this

motion is carried out in the direction of the slit and is supplemented by a rotation of the grating. The movement of the grating may best be performed in two parts: a rough displacement of the entire holder, and a fine motion of the grating within its holder.

The optical effect of this shift is simply a forward-and-backward motion of the Rowland circle in the direction of the normal. If the slit is kept fixed, the change in the focal curve associated with the fixed slit is more complicated. If the shift of the grating is designated by u, then the new distance of the slit will change from $r = r \cos \alpha$ to a value r_u, which can be easily calculated as follows:

$$r_u = \sqrt{u^2 + r^2 \cos^2 \alpha + 2u\, r \cos^2 \alpha}$$

A positive value of u indicates the shift of the grating away from the center of the circle. This value must be introduced in the general formula (49a), and the focus for any value of it can then be determined as long as the effect of error of run is not considered. Since for small displacements u^2 is negligible in comparison with the other members under the square root, approximately:

$$r_u = \sqrt{r^2 \cos^2 \alpha + 2u\, r \cos^2 \alpha + u^2 \cos^2 \alpha}$$

Hence:

$$r_u = (r + u) \cos \alpha \tag{78}$$

This value holds exactly at the normal, and is accurate within $\frac{1}{100}$ per cent for values up to 45°, if u is not larger than $\frac{1}{100}r$. The focal curve of r'_u for the position u is expressed by the use of Equation (75):

$$\frac{\cos^2 \alpha_u}{(r + u) \cos \alpha} - \frac{\cos \alpha_u}{r} + \frac{\cos^2 \beta_u}{r'_u} - \frac{\cos \beta_u}{r} = 0$$

In equally good approximation, from the trigonometrical relations $\sin \alpha : \sin \alpha_u = r \cos \alpha : (r + u)$. Therefore:

$$\sin \alpha = \sin \alpha_u \left(\frac{r}{r + u} \right)$$

and

$$\cos \alpha = \sqrt{1 - \sin^2 \alpha_u \left(\frac{r}{r + u} \right)^2} = 1 - \tfrac{1}{2} \sin^2 \alpha_u \left(\frac{r}{r + u} \right)^2 \cdots$$

Replacing $\cos \alpha$ by $\cos \alpha_u$ yields:

$$\frac{\cos^2 \beta_u}{r'_u} = \frac{\cos \alpha_u + \cos \beta_u}{r} - \frac{\cos \alpha_u}{r + u}$$

$$r'_u \approx \frac{\cos^2 \beta_u r (r + u)}{u \cos \alpha_u + (r + u) \cos \beta_u}$$

$$\approx r \cos \beta_u \frac{(r + u) \cos \beta_u}{(r + u) \cos \beta_u + u \cos \alpha_u} \tag{79}$$

The comparison with the value on the Rowland circle $r' = r \cos \beta_u$ shows that the displaced focal curve originating from the same slit will be located inside of the Rowland circle at the new position of the grating for positive values of u, and that the focal curve will be symmetrical to the normal. The displacement of the grating (or of the slit) is therefore a means of increasing or decreasing the curvature of the actual focal curve. The operation can be used to compensate partially for the error of run over a restricted angle of diffraction. The shift of the slit is also useful for adjusting a second slit on a grating which has already been "rolled" in aberration; the second slit is ordinarily used only for diffracting restricted spectral ranges at higher intensity than is obtainable by the main slit.

66. The Optics of Small Displacements of the Slit

The position of the slit is usually defined by the angle of incidence, which is chosen with regard to the spectral range and order desired. The optimum value of this angle is dependent on the number of rulings per inch and on the specific reflectivity of the particular grating.

The final adjustment of the slit requires only small displacements in the direction to and from the grating, together with the rotation of the slit around the line connecting the slit and the geometrical center of the grating.

A. *The Optical Effect of Small Displacements of the Slit to and from the Grating.* As long as the slit is located near the Rowland circle, the aberrations arising from its displacement are small enough to be negligible unless the maximum resolving power of the grating is desired. To a certain degree it is possible, therefore, to use the changes in the focal curve arising from the displacement of the slit to compensate for the influence of the error of run, or for small deviations in the curvature of the plate holder. However, for grazing incidence, the deviations from the Rowland circle may not be more than minute, since the optimum width of the grating must be used in order to obtain sufficient intensity and resolution.

The increase of the distance from the slit to the grating by the amount s changes the general formula (49a) into the expression:

$$\frac{\cos^2 \alpha}{s + r \cos \alpha} - \frac{\cos \alpha}{r} + \frac{\cos^2 \beta}{r'} - \frac{\cos \beta}{r} = 0$$

Hence:
$$r' = r \cos \beta \; \frac{\cos \beta}{\cos \beta + \cos \alpha - \dfrac{r \cos^2 \alpha}{s + r \cos \alpha}} \tag{80}$$

To a good approximation, if $s \ll r \cos \alpha$:

$$r' = \frac{r \cos^2 \beta}{(s/r) + \cos \beta} \tag{81}$$

Since $r' = r \cos \beta$ holds for the Rowland circle, the value r' becomes smaller for positive values of s, that is, for any displacement of the slit away from the grating. The new focal curve shows, therefore, a decreased radius of curvature, and vice versa: the focal curve will be flattened by a movement of the slit toward the grating. A faulty curvature of a machined plate holder can thus be compensated.

This operation is useful because the lack of definition of the spectral lines arising from a failure of the plate to fit the focal curve is much more pronounced than the lack of definition arising from aberration. How-ever, if the grating is large, and especially at large angles of incidence or diffraction, more care must be exercised.

F i g . 6 7 . Effect of Astig-matism in Line Image When Rulings and Slit Are Not Aligned.

B. *The Rotation of the Slit Around the Light Beam.* When the grating has been adjusted carefully in every degree of freedom described above, so that its "equa-torial" plane containing the Rowland circle goes through the mid point of the slit and through the median line of the plate holder, and the plate holder lies in the focal curve associated with the slit, a final precise adjustment is necessary, especially for attaining the limits of resolu-tion: the slit must be made parallel to the rulings of the grating. This adjustment is necessary because of the astigmatism of the image formation; a limitation in the exactness of this adjustment is set by the curvature of the spectral lines.

As a result of the astigmatism, each point of the slit is imaged on the Rowland circle as a spectral line of length z', where

$$z' = l \left(\sin^2 \beta + \sin^2 \alpha \, \frac{\cos \beta}{\cos \alpha} \right) \tag{52}$$

These lines will be straight in the approximation considered here, and they will be exactly perpendicular to the plane of the Rowland circle. The different points of the slits act in the same manner. If, therefore, the slit is strictly perpendicular to the Rowland plane, the images arising from all its points will be superimposed in the same straight line. If that condition is not fulfilled, the different parts of the slit will give images that are displaced with respect to each other, adding up to a "spectral line" of the form shown in Figure 67. It is evident that the loss of intensity of such imperfect lines may cause trouble and considerably reduce the value of the grating spectrograph.

A rotation of the slit around the axis perpendicular to it and to its jaws will eliminate this trouble. It is, of course, also possible to rotate the grating with its holder correspondingly. However, this operation is more difficult to perform quantitatively because the grating cannot

be turned around the incident beam, but only around its normal, or (still worse) only around the normal of the holder, if the operation of "rolling" the grating has been performed to compensate for the error of run. Since in all cases, when only one grating is to be mounted, the rotation of the slit is possible, the discussion will be restricted to this mathematically much more simple case.

If the slit is inclined by the angle ϕ with respect to a plane through the grating axis L and the mid point of the slit ($z = 0$), then the rays of light passing through points at a distance z from the center of the slit do not have the angle of incidence α, but

$$\alpha_z = \alpha + \frac{z}{r} \sin \phi$$

It is evident that the angle of incidence becomes larger for one direction of z and smaller for the other direction; the sign of ϕ may be taken so that α becomes larger for the positive direction of z, and vice versa. The angle ϕ is so small that $\sin \phi$ can be replaced by ϕ or $\tan \phi$ without loss in the accuracy of the equations.

If the two spectral lines arising from the points z and $-z$ of the slit are considered, it must be noted that their angles of incidence are different, and are given by:

$$\alpha_z = \alpha + \frac{z \sin \phi}{r}$$

and:

$$\alpha_{-z} = \alpha - \frac{z \sin \phi}{r}$$

The two spectral lines, therefore, have different angles of diffraction:

$$\sin \beta_z = \frac{n\lambda}{d} - \sin \left(\alpha + \frac{z\phi}{r} \right)$$

and:

$$\sin \beta_{-z} = \frac{n\lambda}{d} - \sin \left(\alpha - \frac{z\phi}{r} \right)$$

The two direct images are then displaced, since for $\lambda = 0$,

$$\beta_z - \beta_{-z} = \frac{-2z\phi}{r}$$

These two direct images are the centers of two displaced spectra having a difference in position. Substituting $\beta_z = \beta + \delta$ and $\beta_{-z} = \beta - \delta$, in the two equations above, and subtracting,

$$\sin(\beta + \delta) - \sin(\beta - \delta) = \sin\left(\alpha - \frac{z\phi}{r}\right) - \sin\left(\alpha + \frac{z\phi}{r}\right)$$

$$2\cos\beta\sin\delta = -2\cos\alpha\sin\frac{z\phi}{r}$$

Hence:

$$\sin\delta = -\frac{\cos\alpha}{\cos\beta}\sin\frac{z\phi}{r} \tag{82}$$

Since α is always positive, the negative sign on the right-hand side indicates that a line connecting the centers of the spectral lines on the plate is slanted in the direction opposite to the slant of the slit; for $\alpha = \beta$ (Eagle mounting), the amounts of the slant of the slit and of the spectral lines are equal but opposite in direction. The direction of the rotation necessary for the final adjustment is therefore easily seen.

Each spectral line has the length given by formula (52). The centers of the two lines are separated by the amount

$$2z' = 2z\frac{\cos\beta}{\cos\alpha} \tag{83}$$

if the two points on the slit are separated by $2z$. For any angle of emergence β, it is therefore possible to adjust $2z$ to such a value that the length $2z'$ stays just a trifle smaller than the astigmatic length of the spectral lines—thus, the gap in the light between the two spectral lines is completely bridged, each spectral line being elongated so much that it intersects the plane for $z' = 0$. The mathematical expression for this case is as follows; using Equation (52):

$$2z' = 2z\frac{\cos\beta}{\cos\alpha} < l\left(\sin^2\beta + \sin^2\alpha\frac{\cos\beta}{\cos\alpha}\right)$$

$$z < \frac{1}{2}l\left(\sin^2\alpha + \sin^2\beta\frac{\cos\alpha}{\cos\beta}\right)$$

The larger the values of the angle β which are accessible for this test, the larger can be the separation of the two luminous points on the slit; but the general behavior of astigmatism makes it useless to go to angles much larger than about 45°.

A simple calculation shows the sensitivity of this test. The separation $2z$ of the sources on the slit can easily be made 2 cm or more, or as large as the length of the available slit. If the slit is slanted, then the astigmatic elongations of two spectral lines will show some parallel displacement, the amount of which can easily be measured by a measuring microscope. A deviation of 0.003 mm can be detected if the slit is narrow and if the grating is well adjusted in its other degrees of freedom. This deviation arises from two points of the slit that are separated by

2 cm. The least detectable slant of the slit, in first approximation, can then be expressed by the formula:

$$\phi = \frac{.003}{20} = 1.5 \times 10^{-4} \text{ radians} = 30 \text{ seconds of arc}$$

A more accurate calculation can be made by taking into account the fact that the distance of .003 mm on the plate corresponds to the angle 2δ, in the designation used above, according to the equation:

$$.003 \text{ mm} = 2\delta r \cos \beta$$

From Equation (82) is obtained:

$$\delta \cos \beta = -\frac{z\phi}{r} \cos \alpha$$

And therefore:

$$.003 \text{ mm} = -2 z \phi \cos \alpha$$

67. Applications of the Plane Grating

The plane grating is occasionally utilized in special problems where very high resolving power is desired. For such applications, the Littrow mounting is used with a lens of very long focal length and the grating turned to photograph a high order. Lenses of a focal length of 40 feet have been used with the grating set to photograph the sixth or seventh order. With a 6-inch plane grating, with 15,000 lines per inch, in the seventh order the theoretical resolving power is $7 \times 6 \times 15,000$, or 630,000, and such resolving powers have been approximated. A large mounting of this type has been described by Loomis and Kistiakowsky.[12] The development of interferometric devices for obtaining large resolving powers, such as the Fabry and Perot interferometer, has made the application of the plane grating for this purpose less important.

The major use of the plane grating today is in infrared spectrometers, where mirrors are used for collimating and focusing the light. Examples of this type of instrument are given in Chapter 9.

Gratings of a wide range of grating space are used in the infrared. As the wave lengths investigated get longer, it is desirable to use coarser and coarser gratings; the grating constant should always be more than half as large as the longest wave lengths diffracted by it. The wide and deep grooves of the coarsest gratings cannot be successfully cut in speculum metal or in aluminum on glass, and for these coarse gratings soft metals such as copper, tin, or solder have been used.

[12] F. A. Loomis and G. B. Kistiakowsky, *Rev. Sci. Inst.*, **3**, 201, 1932.

R. W. Wood[13] pointed out that if the grooves of a coarse grating could be made with flat sides, a very marked maximum of diffracted energy would occur at angles of observation which coincided with the angles of specular reflection of the incident light. It is clear that, for a particular grating, this effect can be taken advantage of only for a limited range of wave lengths. The grating must be designed especially for the wave-length region to be examined. Wood gave the name of *echelette* to such gratings. Echelette gratings are now used almost exclusively for infrared research and are of great importance because they concentrate the minute amounts of energy radiated by the sources commonly used in this region.

68. Ruling Errors and Ghosts

A perfect grating should have grooves which are straight, parallel, evenly spaced, and exactly identical in form and in depth. Any deviation from these requirements which results in a phase variation of the reunited beams from different grooves by as much as a quarter of a wave length may result in loss of resolving power or in false spectral lines.

Curvature of the rulings introduces an astigmatism in the spectral lines which can be corrected in the focusing of the grating.[14] Lack of parallelism of the rulings in effect results in a variation of the grating space for different longitudinal strips of the grating—hence, a different dispersion for the contributions of the different strips and a loss of definition. Both of these errors arise from a deviation from straightness of the "ways" of the ruling machine. Lack of straightness of the ways is readily investigated and can be held to a negligible amount. These defects should be insignificant.

Error of spacing of the grooves is much more difficult to eliminate. To a certain degree, it is always present and is most troublesome when the spacing errors are systematic, since they then give rise to cumulative effects. Periodic error of spacing arises from a periodic error in the slope of the screw thread of the ruling machine or from an elastic deformation of the parts of the machine which is repeated systematically with each turn of the screw. Great care is always taken to reduce screw error and friction of the ways to a minimum and to evaluate and correct for any remaining periodic error.

Rowland "ghosts." Periodic errors of spacing give rise to false or "ghost" lines in the spectrum. These lie close to the parent line and are symmetrically placed with respect to it. This type of ghost was

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[13] R. W. Wood, *Phil. Mag.*, **20**, 770, 1910; or R. W. Wood, *Physical Optics*, Ch. 7. New York: The Macmillan Company, 1934.
[14] Lord Rayleigh, *Scientific Papers*, **3**, 112.

discovered in 1872 by Quincke and explained in 1879 by C. S. Pierce. Rowland[15] contributed largely to the theory of these false lines and was successful in reducing their intensity to new low levels. Ghosts of this type are now known universally as "Rowland" ghosts. The theory of their formation has been given in numerous places.[16] It is easily shown that about any parent line false lines are produced, with wave lengths:

$$\lambda' = \lambda \left(1 \pm \frac{n'}{nN} \right) \tag{84}$$

where λ is the parent wave length, n the order of the spectrum, n' the order of the ghost, and N the number of lines per turn of ruling-engine
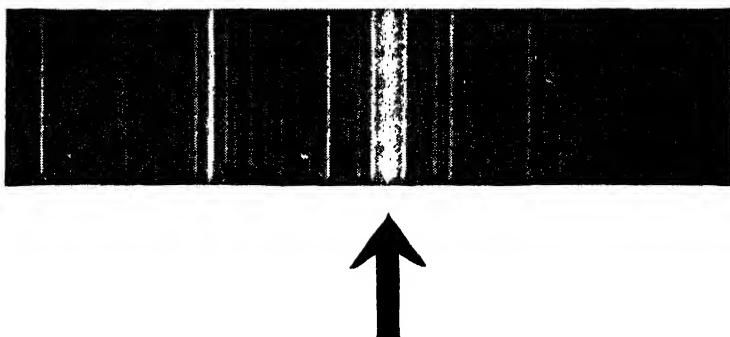
Fig. 68. Rowland Ghosts. The ghost system of the 4047A mercury line is shown. The first, fourth, and ninth ghosts on each side are stronger than their neighbors. A fainter line and its ghost system are mingled with the left-hand ghosts of 4047A.

screw. For Rowland's machine, N was 750, so that in the first order, ghosts appear on either side of the parent line at units of $\frac{1}{750}$ of the wave length, with, in this case, the first, fourth, and ninth orders much stronger than the neighboring orders. In Fig. 68 is shown an example of the ghosts from such a grating. The intensity of the ghosts relative to that of the main line increases roughly with the square of the order of the parent line. It is often given as a working rule that ghosts should not have more than one per cent of the intensity of the parent line in the first order if the grating is to be usable in higher orders.

Rowland ghosts, because of their regular and mathematically calculable spacing, cause little trouble unless they are unusually intense. They may obscure lines close to the parent line, but they need never be mistaken for true lines.

Error of run. Another type of spacing error which sometimes occurs is a progressive variation across the grating either of spacing or

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[15] H. A. Rowland, *Physical Papers*, 525.

[16] J. A. Anderson, *J. Opt. Soc. Am.*, 6, 434, 1922; Meyer, *Diffraction* . . . , p. 174.

of groove form. This error, known as *error of run*, may arise from a
variety of causes, such as temperature change during ruling, progressive
error of the screw, or wear of the ruling diamond. If the error is unsys-
tematic or not progressive across the whole grating, the resolving power
of the grating will be sufficiently damaged, in serious cases, to impair
its value. Progressive error of run is evidenced chiefly by a change in
focal length and focal curve. This effect can be compensated for in the
adjustment of the grating. The procedure is discussed in Section 65.

Error of groove form. Grooves which vary in form and shape diffract
different amounts of light in a given direction with resultant amplitude
differences in the reuniting beams. These amplitude errors are generally
not important in otherwise satisfactory gratings. If they are progres-
sive, this effect is similar to that of progressive error of run. If they
are accidental, they cause scattering of light throughout the spectrum.

Lyman ghosts. A second type of ghost was discovered by T. Lyman,[17]
in 1901; the ghosts lie, not near the parent line, but far from it at wave
lengths which are simple integral fractions of the parent line. Thus,
in Rowland gratings, these ghosts are often found at $\frac{2}{3}$, $\frac{3}{5}$, $\frac{4}{5}$, $\frac{5}{8}$, $\frac{7}{8}$, and
so on, of the main line. The cause of Lyman ghosts has been dis-
cussed by Runge and by Wood, among others.[18] Their cause is not
completely understood, but seems to be due to the superposition of
two periodic errors: one, the periodic error of screw; the other, a periodic
error of much more frequent periodicity. This second periodic error
has been associated with the joint in the driving belt.

Lyman ghosts are generally very much fainter than the parent line,
with $\frac{1}{1000}$ or $\frac{1}{10000}$ of its intensity in good gratings. They seldom
cause trouble except when work is being done in extremely weak spectral
regions, such as the extreme ultraviolet or infrared. In this case Lyman
ghosts of far-off strong lines of the visible region may fall in the region
investigated. Careful tests should be made for Lyman ghosts, which,
unlike Rowland ghosts, may be mistaken for true lines and, in poor
gratings, may be of sufficient intensity to be troublesome.

69. The Testing of Gratings

No perfect grating has ever been ruled. All suffer to a certain extent
from defects of rulings, with resultant scattered light and loss in resolving
power. Since in many cases the performance of a grating can be improved
by determining and masking off defective portions, careful testing of any
newly mounted grating is desirable.

The grating can be examined first for Rowland and Lyman ghosts
without careful focusing. By illuminating the grating with an intense

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[17] T. Lyman, *Phys. Rev.*, **12**, 1, 1901, and **16**, 257, 1903.
[18] W. F. Meggers, C. C. Kiess, C. R. Runge, and T. A. Anderson, *J. Opt. Soc. Am.*,
6, 417, 1922; R. W. Wood, *Phil. Mag.*, **48**, 497, 1924.

mercury arc, or other source with relatively few and strong lines, it is possible to inspect the spectrum visually with the eye placed a few inches back of the focal curve. Lyman ghosts will appear as colored lines in the region between the shortest visible first-order violet lines and the central image. Since the Lyman ghosts repeat the parent lines exactly, this defect can be recognized unmistakably by use of a test spectrum with strong, characteristic doublets or triplets.

Rowland ghosts can be seen if a fine slit is used and the image of a sharp line in the first or second order is viewed with an eyepiece. If the ghosts are at all prominent in the low orders, their intensity relative to the parent line should be determined photographically. This determination may be done approximately by making a series of spectra on the same plate with exposure factors of 1, 100, 300, 1000, and 10,000 and by observing on which exposure the strongest ghosts are as strong as the parent line of the unit exposure. No good grating should have ghost intensities of more than $\frac{1}{100}$ of the parent in the first order; the best gratings will show ghosts of the order of $\frac{1}{1000}$ or less.

It often happens that satellites or diffuse edges will be observed for strong lines at the best obtainable focus. These defects may arise from ruling irregularities in only a part of the grating, and they can then be eliminated or reduced by masking a part of the grating. The seat of such defects can be isolated by making Foucault tests of the grating, by taking "target patterns," or by examining the grating in the light of the defect. The procedure for Foucault tests has been described in Section 41. Complete darkness of the whole grating is not generally obtained with the knife-edge test because of a certain amount of scattered light from groove edges or other irregularities. Any extensive bright areas generally indicate defective ruling, and the effect of masking them should be tested. Foucault tests of gratings have been described in considerable detail by H. G. Gale.[19]

Target patterns are made by photographing a few strong lines, as from a mercury arc, on a photographic plate placed about one-third of the way from the focal curve to the grating. An out-of-focus and much widened line image will be obtained made up of light beams which are converging from the various areas of the grating toward the focus. If all parts of the grating are contributing uniformly to the image, the pattern will show a uniformly channeled structure. A poor grating will produce irregular weak and strong patches because of the irregular diffraction or focusing of light from different areas.[20]

R. W. Wood pointed out that by placing a narrow slit on the focal curve so as to pass only the satellite and not the main line, the grating

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[19] H. G. Gale, *Astrophys. J.*, **86**, 437, 1937.
[20] G. R. Harrison, *Proc. Seventh Summer Conf.*, p. 58. New York: J. Wiley and Sons, 1940.

may then be photographed in the light of the satellite on a photographic plate placed behind this slit, with, if desired, a lens which images the grating on the plate. It can then be determined whether the satellite is formed by beams from only a part of the grating, and if so, these parts may be covered.

The defective parts of gratings are likely to be the first or last parts ruled or the upper or lower edges. Masking such parts reduces the resolving power very little, and, in fact, may improve it by improving the line form. The intensities of Rowland and Lyman ghosts relative to their parent lines are not affected by masking a part of the grating, since all parts of the grating contribute equally to them. All the tests mentioned require some experience in interpretation and are best carried out as comparisons of the test grating with a second grating known to be of superior quality.

70. Cleaning and Care of Gratings

Because any damage to their fine and delicate rulings is irreparable, gratings must be handled with the greatest care and cleaned, if at all, with extreme caution. Fingerprints on metal gratings are hard to remove and likely to cause corrosion. Exposure to any corrosive fumes must be avoided. In vacuum spectrographs, sulphur in gasket rubber or tubing gives rise to dangerous corrosion.

Speculum gratings are subject to oxidation of the surface, which reduces the reflecting power, and to accumulation of dust and grease from the atmosphere. Gratings should be enclosed as completely as possible and covered when not in use in order to retard these processes. Occasional cleaning will, however, be necessary. For cleaning, only camel's-hair brushes or surgical absorbent cotton should be used, and care should be taken to assure that these carry no abrasive particles. All cleaning strokes must be made along the direction of the rulings, and they must be so light as not to damage the rulings. It is safest to use a clean bit of cotton for every stroke.

When loose dust has been removed with a clean brush or cotton, the grating may be carefully swabbed with distilled water. Further cleaning may be undertaken with a dilute solution of ammonia. Ammonia dissolves the oxides, forming blue cuprammonium ion, $Cu(NH_3)_4^{++}$. This treatment, of course, attacks the rulings and should be done with caution. The grating should be immediately rinsed with distilled water.

Another cleaning method for metal gratings which is relatively safe is to flood the surface with collodion. After the collodion surface has hardened, it may be grasped at one corner and pulled off, carrying with it all loose dust and dirt. The stripping may be facilitated by immersing the grating in distilled water.

Gentle rubbing with levigated French chalk wet with alcohol, or, as a last resort, with the finest rouge, is a more vigorous cleaning method but should preferably be done by experienced operators only.

Gratings ruled on glass are not subject to oxidation and can be washed, when cleaning is necessary, with alcohol followed by distilled water, or with alcohol alone. Metal-on-glass gratings must be treated with the utmost care because of the danger of removing the metal coating from the glass. No wet cleaning methods of any sort should be used until it is definitely ascertained by tests on the unruled parts of the metal surface that the metal coating will not be damaged by the treatment.

71. Sensitivity of Grating Spectrographs to Disturbances

Vibrations. The length of the light beams in a grating spectrograph, the fineness of the slit, and the good definition demanded in the spectral lines render the grating spectrograph sensitive to vibrations. Smaller instruments should be constructed very rigidly and should be placed on a heavy pier, preferably with an intermediate layer of a material that will damp vibrations. It is still better to insulate the pier from the floor of the building. Any larger spectrograph should, of course, be used only on the ground floor or in basement rooms. Larger grating mountings should be constructed on many heavy piers, all of which should rest on a single large concrete block which is isolated from the rest of the building by a felt- or rubber-filled space. The thicker and heavier the concrete block can be made, the better. Since the exposure times with gratings extend usually over several minutes, vibrations of brief duration will not be registered. Even prolonged vibration caused, for example, by passing trucks will not displace the light beam from its proper place long enough to make any impression on the photographic plate. The main difficulty arises from continuous vibrations caused by machines or pumps operating close to the spectrograph.

Temperature variations. The temperature in the spectrograph room must be kept constant to a degree that depends on the resolving power desired in the spectra. If the mounting has been properly designed, no perceptible distortion of its parts should occur for slight changes of temperature. The main influence of the temperature is restricted to the expansion of the grating and to the expansion of the air with change in temperature. The two effects partially balance one another. The expansion of the rulings increases the grating constant and, therefore, decreases the dispersion in direct proportion, causing a shift of the spectral lines toward shorter wave lengths, whereas the expansion of the air increases the wave length of the spectral lines.

If the grating is made of speculum metal, the expansion of the grating produces the predominant effect. Since speculum metal has an expansion coefficient of 1.9×10^{-5} per Centigrade degree, a desired resolving power

of 100,000 restricts the allowed temperature variation to about one-fifth of a degree Centigrade. Any larger shift will damage the resolution. If a higher or lower resolving power is used, the variation of temperature permissible during an exposure will be proportionally smaller or larger. The influence of the expansion of the air is less than that of the expansion of the grating. A rise of 1°C in the temperature of the air corresponds to a dilution of the air by one-third of one per cent. Since the wave lengths in vacuum are about 1A higher than those in air (see Section 84), a temperature rise of 3°C will change the wave lengths by $\frac{1}{100}$A. This change corresponds, at wave lengths of 3500A, to a shift of 3×10^{-6} in $d\lambda/\lambda$, and would damage a resolving power of 100,000 or better.

For gratings ruled on glass, the thermal expansion coefficient is about one-half as large (9×10^{-6} per degree Centigrade) as for speculum, while for Pyrex it is only one-sixth as large (3×10^{-6} per degree). The expansion of the grating, even for Pyrex, causes an effect three times as large as the shift resulting from the expansion of the air. However, for gratings ruled on quartz, the temperature effect on the spectral lines is due primarily to the shift caused by the expansion of the air, since this amounts to $d\lambda/dT = 10^{-6}$ angstroms per degree Centigrade (for the usual spectral range), whereas the thermal expansion coefficient of the grating is only 0.4×10^{-6} per degree Centigrade.

The temperature changes mentioned are those resulting from a slow shift in the uniform temperature of the whole apparatus. Much more disturbing is a lack of uniformity in the temperature of the spectrograph which causes air currents in the light paths. These air currents and eddies may act like lenses, refracting the light beam to a curved path and so causing a bad blurring of the photographed spectral lines. A difference in temperature between the spectrograph room and the adjoining source room may cause air currents to flow through the slit; a temperature gradient may thus be formed at a small angle to the line of sight through the slit which will have the optical effect, as seen from the grating, of a virtual shift of the slit. Such air currents through the slit may seriously affect the resolving power and should be avoided. The spectrograph room should be as nearly as possible hermetically closed; in cases of persistent draft, it may be advisable to provide bypasses for the air or to cover the slit by a thin quartz plate. Smaller grating spectrographs will usually be faster, and their lower resolving power may permit a temperature shift of half a degree during the exposure, a condition which can be maintained in most laboratories. Larger spectrographs can be surrounded with a heat-insulating layer of Celotex. The largest spectrographs require the maintenance of temperature control within 0.1°C, and this control is best attained by mounting the grating in a basement room if possible, and by utilizing delicate thermo-regulators to hold the

room temperature at a fixed point, which must, of course, be higher than the maximum normal room temperature.

Changes in the barometric pressure. Since the refractive index of air is 1.0003, a change in the barometric pressure of one inch produces a wave-length shift of one part in 10^5. For the best concave gratings, a resolving power of 300,000 has been attained. A shift of the barometric pressure of one-third of an inch during an exposure will then shift the principal maximum of a spectrum line from such a grating to the position of the first diffraction minimum. The resolution of two lines separated by $\lambda/d\lambda = 150,000$ would therefore be completely destroyed, since the intensity minimum of their pattern lies halfway between the lines. It is not feasible to keep the air pressure constant in large spectrograph rooms, as was done by Urey for medium-sized prism spectrographs. Another method which has been applied to prism spectrographs consists of compensating for the pressure shift of the spectral lines by introducing a controlled shift in the opposite direction by means of a plane parallel quartz plate that is placed between the slit and the collimator lens. The principle may be best understood by tracing the beam path backward from the spectral line to the slit. The spectral line must always be imaged at the same position on the photographic plate. With a change of barometric pressure, the angular deviation introduced by the prism changes, and the ray, in order to reach the desired position on the plate, can then no longer originate at the slit but must come from a slightly shifted slit position. The inserted quartz plate should be perpendicular to the beam in the initial condition of pressure. By rotating the plate around an axis parallel to the slit, it is possible to displace the ray from the prism by an amount that will compensate for the apparent shift of the slit.

An automatic device has been described by Beutler and Fred[21] which uses this principle and is suited for use with large grating spectrographs. The thin crystal quartz plate must have optically flat and parallel faces; it is inserted directly behind the slit and is rotated about its optical axis, which is parallel to the slit. The barometric pressure acts on a sylphon bellows of suitable rigidity connected to a lever pivoted at the axis of rotation of the plate and rigidly attached to the plate. The length of the lever is adjustable to provide the required rotation for the particular wave length and order at which the spectrogram is to be taken. The value of the angle by which the quartz plate has to be rotated depends, of course, on the thickness of the quartz plate, which should be as thin as possible for purposes of keeping the astigmatism at less than one-fourth of a wave length. The calculation of the dis-

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[21] H. Beutler and M. Fred, *Phys. Rev.*, **57**, 69, 1940.

placement of the beam yields the formula

$$x = t \sin \rho \left(1 - \frac{\cos \rho}{\sqrt{n^2 - \sin^2 \rho}} \right)$$

where t is the thickness of the plate, ρ its angle of rotation from the normal, and n the refractive index. The mechanical arrangement is such that the tangent of the angle of rotation ρ is proportional to the change in the barometric pressure, since under this condition the parallel displacement of the light beam

$$x = t \tan \rho \left(\frac{n - 1}{n} \right)$$

has the desired value (within 1 per cent) up to rotations of 35° of the quartz plate. By this device, pressure changes up to plus or minus one inch during one exposure are automatically taken care of. The device offers the possibility of starting the exposure with the compensating plate at any desired angle to the light beam, thereby anticipating any change in the barometric pressure that may be predicted by the weather bureau. It is, of course, advantageous to have the plate perpendicular to the light beam for as much of the time as possible. The sylphon bellows is connected to the outside air by a stopcock that permits equalization of the pressure at the beginning of the exposure. Concerning the mechanical details, and the arrangement of ball bearings for minimizing friction, the original article should be consulted.

It is, of course, necessary to readjust the position of the slit after introduction of the quartz plate for the change in the optical path; the slit must be moved away from the grating by about $(n - 1)t$. Compensation is perfect for only one wave length; however, for a wave-length range of ± 10 per cent, there is still better than 90 per cent correction; and for the extreme case of working in different orders simultaneously, it is still better than no correction, by the factor three.

72. Light Losses and Stray Light in Grating Spectrographs

Light losses in spectrographs were discussed in Section 43. Although the principles were applied there chiefly to prism spectrographs, they hold equally well for grating instruments.

In the case of Rowland mountings of the concave grating, the only optical part in the light beam is the grating itself, and the only light loss is at the grating. The light actually lost in reflection may be very small in the infrared and visible regions, where the reflecting power of the usual grating materials, if clean, is 90 per cent or more. For the vacuum region, and particularly below 500A, the reflection loss at the single reflection may be very large. Glass and aluminum, although relatively poor reflectors of visible light, are often used as grating materials in this

region, since aluminum has the best reflecting properties in the extreme ultraviolet, while glass has reasonably good reflecting powers and is favored because of its smooth ruled surface.

For Wadsworth mountings of the concave grating, or for plane grating mountings, with their associated mirrors or lenses, the considerations of Section 43 may be applied directly in considering the losses in these additional optical parts.

Stray light in spectrographs was discussed in Section 44 under the headings of leakage, reflection and scattering from the walls and optics mountings, reflection and scattering from the surfaces of the optics, and scattering and fluorescence within the optics. The same phenomena may arise in grating spectrographs. As noted in the discussion of light losses, the grating spectrograph has in general fewer optical elements and surfaces to scatter and reflect light.

The grating itself scatters a certain amount of light in an irregular manner because of scratches and roughness in the grooves, or because of material piled up between the grooves by the ruling point. In good gratings, the amount of light scattered by the optics is far less than in prism spectrographs. Because of the irregular nature of the scattering, it is, however, usually not possible to reduce the effect of the scattered light on the photographic plate by diaphragms or other devices.

It should be remembered that, while, in the case of prism spectrographs, all light which is not lost by reflection or scattering finds its way into the single refracted spectrum, such is not the case for a grating. With a grating, a certain amount of light is specularly reflected into the direct or zero wave-length image. The amount of light in this image is dependent on the amount of surface of the blank left between the rulings.

The distribution of light among the different orders and on the two sides of the normal is largely influenced by the shape of the grooves. For the ideal case of a grating with alternate opaque and transparent strips of equal width, the distribution of light should be uniform on each side of the normal and the intensity of successive orders should decrease in the inverse ratio of the squares of the successive odd integers: as 1, $\frac{1}{9}$, $\frac{1}{25}$, and so forth. In any actual grating, however, the rulings have a finite width and a definite shape, usually in the form of a flat trough with unequal angles for the two sides. The flat sides of the grooves tend to reflect light specularly in two definite directions, so that in these two directions on either side of the normal the spectra will be much stronger than elsewhere. Gratings will be chosen, if possible, so that the desired wave-length range and order, $n\lambda$, fall along a preferred direction. Thus, a grating with a strong first-order visible spectrum at 5000A should have a strong second-order spectrum at 2500A. This effect is purposely exaggerated in echelette gratings (Sec. 67). R. W. Wood succeeded in ruling gratings for use in the visible and photographic

regions in which the light is largely concentrated in one order on one side of the normal. It is possible for such a grating to throw 80 per cent or more of all light into the first-order visible spectrum.[22] Such a grating may exceed a prism in the brilliance of its spectra. When it is possible to produce such gratings in commercial quantities, they may, because of their convenience and simplicity, supersede prisms to a considerable extent.

For gratings ruled in the ordinary manner with a sharp diamond point of unselected angle, it is generally not possible to predict in advance upon which side of the normal the spectra will be brighter, or whether the intensities of successive orders will decrease in a regular manner. It is necessary to determine these questions by observation, which can usually be done visually.

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[22] Wood, R. W., *Physical Optics*, 3rd ed., p. 264. New York: The Macmillan Company, 1934; *Nature*, **140**, 723, 1937; H. D. Babcock, *J. Opt. Soc. Am.*, **34**, 1, 1944.

CHAPTER 8
The Photographic Process

The importance of the photographic process in spectroscopy depends on two basic facts: it is cumulative, and so extremely weak radiations may be recorded by prolonged exposures; it results in a permanent record which can be examined and measured at leisure and preserved for future study or reference.

Photographic image formation rests not only on the fact that the silver halides are photosensitive, but also on the fact that the action of light on silver halide crystals produces a latent effect which may remain for days, or even years, and which makes it easier to liberate silver from the compound where it has been acted on by light than where this action has not occurred. This liberation is performed by suitable reducing agents or *developers*, which leave metallic silver in the form of the image; the unreduced silver halide is removed by the aid of a solvent or *fixer*, usually sodium thiosulphate or *hypo*.

73. The Photographic Emulsion

In practice, the light-sensitive silver salts are used in the form of an *emulsion*—a suspension of small crystals in gelatin which holds the crystals in position and which is transparent to light of a wide range of wave lengths. The emulsion is spread in a thin layer on a support—commonly glass, cellulose-ester film, or paper. The gelatin film, when wet, swells only in the direction perpendicular to the support; the swelling is several times the original thickness. The swollen gelatin is readily permeable to water and to water solutions, such as developer and fixer, and so is readily processed. Finally, when dry, the gelatin returns to almost exactly its original form and position. All these properties make gelatin a nearly ideal medium for photographic purposes.

The silver salts commonly employed are the chloride, the bromide, and the iodide. The bromide is the most sensitive and has the widest color-sensitivity range. In all negative emulsions, it is used pure, or with a small percentage of iodide. In the slower, positive emulsions the chloride, the bromide, or mixtures of the two are used. The process of preparing and coating the emulsion is rather complicated and, to some extent, a trade secret. Various procedures are used to control the hardness of the gelatin, and the speed and other characteristics

of the finished product.   The larger monographs listed at the end of this chapter should be consulted for more detail.

74. The Silver Grain and the Latent Image

The sensitive coating of emulsion has a thickness of from a few thousandths to 30 or 40 thousandths of a millimeter.   The crystals or *grains* of silver halide are scattered through this gelatin sheet.   The grains are usually flake-shaped and tend to orient themselves approximately parallel to the plate.   They vary in size from the submicroscopic to an upper limit of 6–8μ in diameter.   There is a distribution of sizes in any emulsion, with a most frequent area, usually of 0.1–0.2 square microns; in slow and fine-grained emulsions there is a closer grouping around this size than is present in fast and grainy ones.

The silver grains, when struck by light of suitable wave length, become sensitized so that they are more readily reduced to metallic silver than are the unexposed grains.   The aggregation of these sensitized grains in an emulsion constitutes the *latent image*, which is developable to a photographic image.   The exact nature of the latent image is not clearly understood, in spite of much study and speculation.   Of the various theories proposed, the most successful is the silver-germ sulphide-speck hypothesis, as interpreted in terms of the modern quantum theory of crystals.[1]   This theory holds that the development nuclei of the grains are silver sulphide specks, present in the halide crystals as impurities.   This sulphide may come from atmospheric sulphur (H_2S), from the gelatin from animals which have fed on wild mustard (mustard oil—$CH_2{:}CH{:}CH_2NCS$),[2] or from mustard oil artificially introduced in the manufacture of the gelatin.

The sulphur atoms in the crystal provide localized energy levels higher than those of the halide atoms.   The absorption of light by the crystal raises electrons from the halide atoms to crystal levels, in which they may move through the crystal until trapped by the localized sulphur levels.   The sulphide specks thus become negatively charged and tend to collect free silver ions into silver nuclei, which are centers for development and constitute the latent image.   The original papers should be consulted for details.[3]

75. Properties of the Emulsion—The Characteristic Curve

The major physical properties of an emulsion are speed, contrast, latitude or useful range of exposure, graininess, and spectral sensitivity.

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[1] R. W. Gurney and N. F. Mott, *Proc. Roy. Soc.*, **164A,** 151 (1938); J. H. Webb, *J. Opt. Soc. Am.*, **26,** 367 (1936).

[2] S. E. Sheppard, *Phot. J.*, **65,** 1 (1925); *J. Soc. Motion Picture Engrs.*, **24,** 500 (1935).

[3] A good review is given by J. H. Webb, *J. App. Phys.*, **11,** 18 (1940).

They are not all mutually independent. Other physical properties, such as halation, turbidity, resolving power, intermittency, and reciprocity-law failures are also important, and these, likewise, are not wholly independent of each other or of the former.

The first three of the major properties of the emulsion are obtainable from the characteristic curve of the emulsion (Fig. 69), which shows the relationship between the light exposure (on a logarithmic scale) received by the emulsion and the resultant density of the developed image. Exposure is measured, usually, in meter-candle-seconds, and density is $\log_{10} I_0/I$ (I_0 is incident light intensity in the photometering beam; I, that transmitted by the plate; and $I_0/I = 0$, opacity). This curve will be recognized as exhibiting, up to its maximum value, a
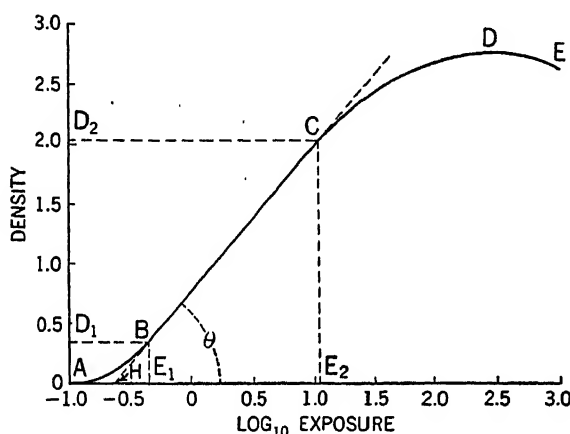
Fig. 69.   The Characteristic Curve of a Photographic Emulsion.

form often seen in graphical representations of statistical behavior where the total effect produced in a large number of individual cases is plotted against the value of the factor responsible for the effect. Examples are the magnetic curve of iron, the curve of plate-current versus plate-voltage of a vacuum tube, and the curve of the fraction of a given population which will have died at any age, versus age. In the case of an emulsion, since density is dependent on the number of grains which have been developed or blackened, the curve represents a plot against the light exposure of the number of grains which require, for blackening, not more than a given exposure. The decrease of the density beyond the maximum, known as *reversal* or *solarization,* is to be attributed to the entrance of a new phenomenon.

It will be seen that the curve begins at a point A, the *threshold exposure* at which blackening first becomes perceptible. A curved toe AB is then followed by a considerable region BC, where the curve is nearly straight—density increasing linearly with exposure. A knee CD, a

region of decreasing response to exposure, is followed by a region DE of reversal of density.   The intersection H of the exposure axis with the straight-line portion BC of the characteristic curve determines an exposure the logarithm of which is OH, known as the *inertia* of the plate.
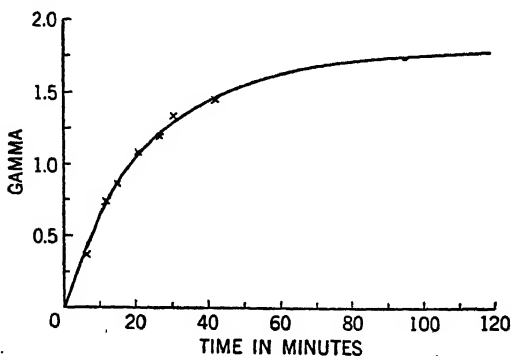
Fig. 70.   The Variation of Gamma with Time of Development.

The slope $\tan \theta$ of this straight line is known as the development factor of the emulsion and is generally denoted by γ (*gamma*).

$$\gamma = \tan \theta = \frac{D_2 - D_1}{\log E_2 - \log E_1}$$

If $\gamma = 1$, density increases in direct proportion to exposure, a condition which is necessary for proper relative reproduction of different luminous intensities in different parts of a picture.   It may be noted that the slope, or γ, is independent of the units used in measuring exposure, since, in a logarithmic curve such as the characteristic curve, change of units merely shifts the curve parallel to itself without change of slope.   The γ for a given emulsion does change, however, with the degree of development, increasing rapidly at the start and then less and less rapidly as development continues, until the maximum attainable value, γ_∞, is reached

Fig. 71.   Characteristic Curves for the Same Emulsion at Different Stages of Development.   The upper curve is for a later stage of development than the lower, but its linear portion tends to intersect the log E axis at the same inertia point, H, as does that of the lower curve.

(Fig. 70).   With most negative emulsions, and with developers without much bromide, the straight part of the characteristic curve tends to

rotate about the point H, for a series of curves taken at various stages of development (Fig. 71). With much bromide in the developer, the intersection point may be below the log E axis, and with photographic papers the characteristic curves tend to shift toward the left without much change in γ for increased development time.

With negative emulsions, then, it is possible, by stopping development at a time when $\gamma = 1$, to obtain proper relative-contrast reproduction if the positive emulsion or the printing paper is also developed to a gamma of 1. In pictorial photography, it is desirable to stop development at this point. In spectrum photography, unit gamma is not so essential. Development is often carried on until the appearance of background fog checks the increase in contrast. For microphotometric purposes, it is usually desirable to use a development routine that will produce nearly the same gamma on each plate.

76. Emulsion-speed Rating Systems

Fundamentally, the speed of an emulsion is measured by the exposure necessary to produce a given opacity; hence, it can be read from the characteristic curve. Since, however, emulsions differ both in inertia and in gamma, and high inertia often accompanies high gamma and vice versa, the more sensitive of two emulsions at low exposures may not be the more sensitive at higher exposures. For example, in Fig. 72, emulsion A has a lower inertia than emulsion B, and would record faint sources of light with a shorter exposure than would B. On the other hand, if a certain minimum

Fig. 72. Characteristic Curves of Two Different Emulsions, Showing Differences of Relative Speeds.

density of 0.5 or more is wanted, as is often the case in spectroscopic work, emulsion B is considerably faster than emulsion A.

Several systems of rating emulsion speeds have been proposed and used; but since some compare emulsions in threshold speeds, and some in the relative speeds at higher densities, the various systems are not wholly comparable and do not rank emulsions in the same order. Furthermore, some of the systems use a linear scale, so that double the index number indicates twice the speed, while others use a geometric or logarithmic scale.

An early and well-known rating system is that proposed by Hurter and Driffield (1890) and known as the *H and D number system*. These

numbers are inversely proportional to the inertia values and are obtained, in the Continental H and D system, by dividing 34 by the inertia value in meter-candle-seconds, and, in the American H and D system, by dividing 10 by the same inertia.   On the basis of the American system, available emulsions range from contrast or lantern-slide plates, with ratings of from 5 to 10, to high-speed panchromatic materials, with ratings as high as 1000–1500.

The H and D numbers depend both on the slope and on the position of the straight part of the characteristic curve, and ignore the threshold and toe of the curve.   It is possible that two emulsions, with quite different values of threshold illumination or of illumination required to produce low densities, could have identical inertias and H and D numbers, or, conversely, that they could have the same H and D number and require quite different exposures to produce densities of the order of 1.0.

The Scheiner numbers, which have been much used in Europe, are speed ratings based on the exposure necessary to produce, under fixed conditions, a minimum perceptible blackening of the emulsion.   They measure the threshold exposure, on the assumption that a low threshold exposure indicates a fast plate.   The numbers themselves have a logarithmic scale, for which the base is 1.27 in the American Scheiner system and 3.03 in the Continental Scheiner.   Ordinary emulsions range from 1° American or 6° Continental, for slow emulsions, to 20° American or 25° Continental for fast ones.   The system is open to the objections that it does not quantitatively specify the density which corresponds to a minimum perceptible blackening, and that it rates the emulsions on their behavior in the region of underexposure, assuming that their response in the ranges of useful exposure will be in the same order of speed.

A speed rating that has recently attained much popularity is the Weston system.   The Weston number is defined as $4/E_w$, where E_w is the exposure in meter-candle-seconds necessary to produce a density numerically equal to gamma, with standard development as recommended by the manufacturer.   This system has the advantage that it compares the emulsion speeds at densities in the usual range.   For most emulsions, however, if a density of gamma lies on the straight part of the curve, the exposure E_w is very nearly ten times the inertia exposure. The Weston numbers are, then, about $\frac{1}{25}$ of the American H and D numbers, and so range, for ordinary emulsions, from about 0.5 to 64.

A new method of rating emulsion speed has been proposed by the Subcommittee on Sensitivity to Radiant Energy of the Committee on Standardization in the Field of Photography of the American Standards Association.[4]   The specifications for exposure and processing are given

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[4] *J. Opt. Soc. Am.*, **31**, 87, 1941; **33**, 479, 1943.

in detail.   Briefly, after the emulsion has been exposed in a non-inter-
mittent, intensity-scale sensitometer to a one-candle-power source of
radiation, consisting of a tungsten lamp, at a specified temperature, and a
liquid filter, and after a carefully specified processing technique has been
followed, the densities are measured and plotted against log exposure.
As in all sensitometry, the density plotted should be the density above
clear-plate density.   A log exposure range of 1.50, AB in Fig. 73, is
then moved along the axis until a position is found such that the slope
of the curve at the low end of the range, tan α, is 0.30 of the average slope
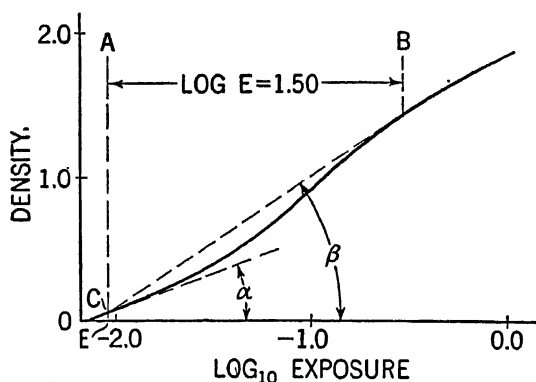
Fig. 73.   Characteristic Curve Illustrating the Speed Numbers of the American
Standards Association.

over the entire range, tan β.   The exposure E, corresponding to the
point C at the low end of the range, is used to compute the Speed S, and

$$S = \frac{1}{E}$$

It is suggested that the value of $1/E$ be preceded by a zero to dis-
tinguish this speed criterion from others.   Thus, if $\log_{10} E$ is 7.90,
$\log_{10} 1/E = 2.1$, $S = 125$, and the Speed is given as 0125.

The Speed designation may be used when this sensitometric criterion
for calculating speed has been used.   If, in addition, exposure, processing,
and evaluation of the emulsion have all been carried out in strict accord-
ance with the outlined specifications, the Speed may be further character-
ized by the initials ASA (American Standards Association): for example,
ASA Speed 0160.

A rating of a film for use in connection with exposure meters and
exposure tables is obtained by dividing ASA Speed by 4.   The resulting
values are called *Speed Numbers* and are found to correspond to the
numbers commonly used in such meters and tables,

$$\text{Speed Number} = \frac{\text{Speed}}{4}$$

It will be seen that this system takes account of the lower curved part of the characteristic and uses as its reference point the exposure at which the rate of increase of density has become a large enough fraction of the gamma of the straight part to insure a photograph with adequate contrast in the underexposed parts of the picture. It thus measures the exposure necessary to reach a minimum useful gradient of density and so lead to an excellent print.

All emulsion speed numbers depend to a considerable extent on the particular light source used for the exposures, since the various emulsions vary widely in their spectral sensitivity. Daylight has a higher color temperature than a tungsten lamp has and is a bluer light. Accordingly, nonpanchromatic emulsions appear relatively faster in daylight than in tungsten light, while panchromatic materials are less affected.

77. Emulsion Latitude

The *useful exposure scale*, or *latitude of the emulsion*, is the ratio of the maximum to the minimum exposure which will give satisfactory reproduction. In pictorial photography this range is essentially limited by the length of the straight part of the characteristic curve. This linear exposure scale may vary from only 5 to 10 in process emulsions of high gamma to 250 or more in portrait emulsions. The exposure latitude in any particular case is the ratio of the useful exposure scale of the emulsion to the range or scale of brightness of the object photographed. If this ratio is less than one, it is impossible to photograph the object with correct tone value for all parts. Above the ratio of one it is possible, and the greater the ratio, the easier it is, to make a photograph in which the exposure for all parts falls on the straight part of the curve. In spectrum photography, especially if density measures are to be made by photometer rather than by eye, it is not essential that only the straight part of the characteristic curve be used. However, for best discrimination between small intensity gradations, and hence for best accuracy in intensity determinations, it is desirable to work in the linear region and to use an emulsion of as large a gamma as will still give this latitude.

78. Emulsion Graininess

On examination under a microscope, all photographic emulsions, after exposure and processing, show a granular structure or *graininess*. This granularity depends in part on the size of the original silver halide particles, but to a much greater extent on the aggregation or clumping of the grains which results from development. The amount of this clumping depends, in turn, partly on the original grain size and partly on the developer used. Low-granularity or fine-grain developers can decrease the graininess by something like a factor of two from that produced by general-purpose developers.

Objective quantitative methods of measuring plate graininess have been devised.[5]　However, graininess is not one of the fundamental emulsion constants, although it is one of the factors influencing resolving power.　It is, therefore, usually sufficient to have qualitative information on the relative graininess of different emulsions.　Dunham[6] has pointed out that such comparisons can be conveniently made from microphotometer tracings of emulsion regions uniformly blackened to a density of 0.3. Figure 74 shows such tracings for several Eastman Kodak Company emulsions often used in spectroscopy.　The emulsion area covered by the

KODAK 50	TYPE Ia-O
KODAK 40	TYPE 103
KODAK 33	TYPE I
KODAK PROCESS	TYPE II
KODAK SUPER ORTHO PRESS	TYPE III
KODAK SUPER PANCHRO PRESS	TYPE IV
KODAK PANATOMIC X	TYPE V

TYPE 548
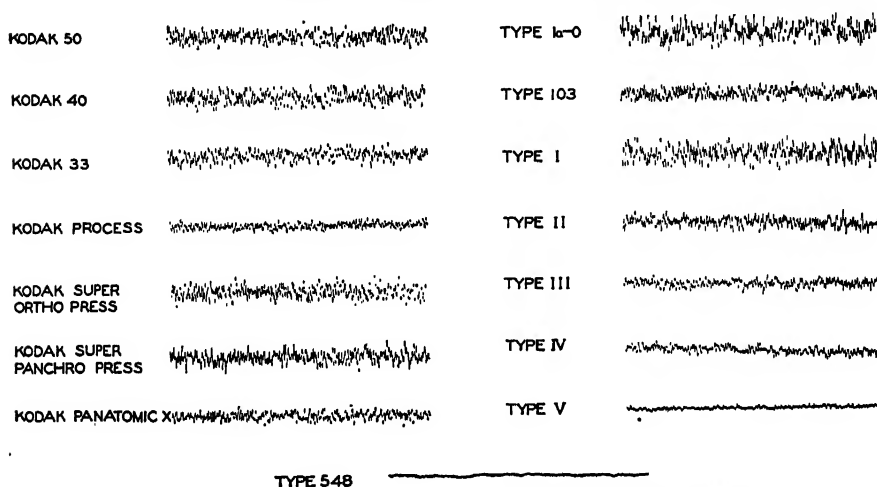
Courtesy of the Kodak Research Laboratories.

Fig. 74.　Relative Graininess of Selected Photographic Emulsions Illustrated by Microphotometer Tracings.

microphotometer slit is 0.5 mm in length and 5μ wide.　The irregularities indicate variation in grain along the plate.

79. Spectral Behavior of Emulsions

The properties of all photographic emulsions show dependence on the color or wave length of the light used.　The silver halides all have sensitivity maxima in the blue or violet parts of the spectrum: silver chloride at about 3800A, silver iodide at about 4200A, and silver bromide at about 4800A.　Their respective sensitivities fall off sharply toward the red but slowly toward the violet, and, in fact, they are sensitive down to the shortest known wave lengths.　(The failure of plates in the short-wave-length ultraviolet is due to the opacity of gelatin in this region.) It was discovered by Vogel,[7] in 1873, that the range of sensitivity of an

[5] A. van Kreveld, *J. Opt. Soc. Am.*, **26**, 170, 1936; A. Goetz and W. O. Gould, *J. Soc. Motion Picture Engrs.*, **29**, 510, 1937.

[6] T. Dunham, *Proc. 8th Int. Phot. Congress*, Dresden, 1931.

[7] H. W. Vogel, *Pogg. Ann.*, **150**, 453, 1873.

emulsion could be extended toward the red by staining it with a suitable dye.   Dyes are now widely used for this purpose, and dyed emulsions

Courtesy of the Kodak Research Laboratories
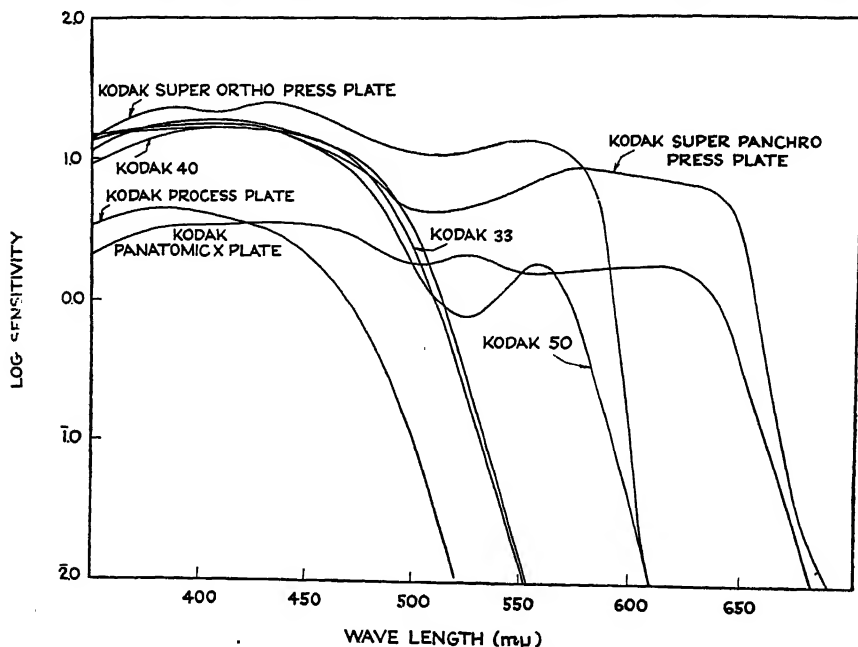
Fig. 75.   Variation of Sensitivity with Wave Length of Selected Photographic Emulsions.

are called orthochromatic when sensitized up to the green and yellow, panchromatic if sensitized into or through the visible red, and infrared-sensitive if the sensitivity extends into the invisible infrared.

Characteristic curves must be taken for various wave lengths, or wave-length bands, to show the spectral behavior of an emulsion. The exposure cannot be expressed in meter-candle-seconds, because this unit refers to a white or undispersed light; it is usually expressed in some absolute unit, such as ergs per square centimeter. The variation of sensitivity with wave length for different emulsions is shown in Fig. 75. Sensitivity in this case is measured in absolute energy required to give a density of 0.6 when the emulsion is developed to a fixed gamma. The

Fig. 76.   Variation of Gamma with Wave Length for a Selected Photographic Emulsion.

variation of gamma with wave length for a typical emulsion is shown in Fig. 76. It will be noted that both sensitivity and gamma vary rapidly and widely with wave length. For spectrographic purposes, it would be desirable to have an emulsion of uniform characteristics throughout its whole useful range. Since such emulsions are not available, it is necessary, for quantitative work, to calibrate the emulsion, or the spectrograph and emulsion, for comparison of different wave-length regions. (See Sec. 99.)

80. Resolving Power of Emulsions

An important characteristic of photographic emulsions is their resolving power, or ability to reproduce fine detail. Emulsion resolving power is usually measured by the number per millimeter of uniform black lines, separated by white spaces of equal width, which can just be resolved. Resolving power is dependent on a number of factors. Graininess, which might seem at first sight the most important, is one factor: coarse-grained plates generally have lower resolving power than fine-grained ones. The immediately important factors, however, are turbidity and contrast.

Turbidity is the spreading of the image size with increasing exposure. In coarse-grained plates, this spreading is largely due to the reflection of light by silver grains, and is thus independent of wave length; in fine-grained plates, diffraction-scattering predominates, and, of course, decreases rapidly with wave length.[8] The scattering, in either case, is affected by the penetration of light into the emulsion, being greater with greater penetration and so less in emulsions which absorb light strongly.

Resolving power also is greater in emulsions of high contrast, because high contrast aids in the sharp differentiation of close lines. Since fine-grained plates usually have high contrast and low turbidity, high resolving power usually is associated with such plates. Furthermore, since grain and contrast are influenced by the type of developer and development technique, resolving power can be affected by development. Resolving power, as usually reported, varies from 40–50, for high-speed emulsions, to 100–150 for the finest-grained plates: from the figures previously given on grain size, page 184, it will be seen that the narrowest resolvable line width is still many times the average grain size.

81. The Reciprocity Law

For quantitative spectroscopic purposes, it is necessary to know how the response of the emulsion is affected by the intensity, constancy, and continuity of the incident light. It is generally assumed that the response of the plate depends only on the total energy per unit area which strikes the emulsion; accordingly, *exposure* is defined as the product of the

[8] C. E. K. Mees, *Proc. Roy. Soc.*, **83A**, 10, 1909.

accelerators, restrainers, and sometimes special compounds such as hardeners, clarifiers, toning agents, or grain-size reducers.

Not all organic reducing agents are developers, since not all possess the power to discriminate between exposed and unexposed silver halide and so reduce the latent image while leaving the remaining silver grains nearly or wholly unaffected. Since the discovery in 1851 of the developing action of 1:2:3-trihydroxybenzene (pyrogallol), more than one hundred developers have been found; only about a dozen, however, are in common use today. The most common of these are pyrogallol (pyro). glycine, hydroquinone, metol (elon), *p*-phenylenediamine, and *p*-aminophenol. Various salts of the two last-named reducers, such as the sulphate and hydrochloride, are also used as developers: metol is, in fact, methyl-*p*-aminophenol sulphate; the popular Rodinal is *p*-aminophenol hydrochloride.

Developing agents are rated in activity by their reduction potential or ability to overcome the restraining action of potassium bromide. Hydroquinone is arbitrarily rated as 1.0; the agents mentioned above are rated as follows:

p-Phenylenediamine hydrochloride, no alkali	0.3
Hydroquinone	1.0
Glycine	1.6
p-Aminophenol	6.0
Pyrogallol	16.0
Metol	20.0

Developing agents also differ widely in characteristics other than speed, for example, keeping properties, staining of emulsions or fingers, tonal color of negative, grain size, production of background fog, and effect on emulsion contrast. Pyro, for example, keeps poorly, is slow, produces low contrast, stains emulsion and fingers yellow-brown, and gives a brownish, soft image which, although often favored in portrait work, is not desirable in spectroscopic work. Hydroquinone is a slow, high-contrast developer and keeps fairly well; it is most often used in combination with other agents, chiefly metol, or with caustic soda. Glycine is, of common developers, the most resistant to oxidation and produces a fine-grained image with very little fog. *p*-Aminophenol is convenient to handle because of the high concentration of the stock solution, is rapid, and is one of the best developers in warm solutions and, hence, for use in warm or tropical climates. Metol is a vigorous, very stable, low-contrast developer, used mostly in combination with hydroquinone in a wide range of proportions to give various degrees of contrast. *p*-Phenylenediamine is a very weak developer, with a toxic action on some skins, and is useful chiefly because of its tendency to give a very fine grained image. It is often combined with more active developing agents.

An important function of the hydroquinone in metol-hydroquinone formulae is to preserve the metol from oxidization. All developing formulae include some preservative—the most common is sodium sulphite or bisulphite—and its action is almost essential to the life of the solution. The sulphite has the effect also of increasing the activity of the developer and of dissolving the surface of the silver halide grains, so tending to prevent clumping in large grains.

An alkali is usually added to the developer to increase the activity or speed of the formula, since most developing agents have little or no activity in neutral or acid solutions. The most common such "accelerator" is sodium carbonate, although borax is used in slow, soft developers and caustic soda in high-speed, high-contrast developers.

Developing formulae almost always contain a restrainer or anti-fogging compound which increases the ability or tendency of the developer to reduce the silver halide of the latent image without affecting the unexposed halide. By this means, background or fog is kept down—an extremely important consideration in spectrographic work. Although all the alkali halides and numerous organic compounds have a restraining effect, potassium bromide is by far the most common restrainer.

The four components discussed—developing agent, preservative, accelerator, and restrainer—make up the usual developing formula. Some other compounds may be added for special purposes. All manufacturers of plates and films supply formulae for developers recommended for use with their emulsions. For general spectrographic purposes, the most popular developers are high-contrast metol-hydroquinone formulae such as Eastman Formula D19 or D72, or, when high-speed as well as high-contrast development is wanted, hydroquinone-caustic formulae, such as Eastman D8.

Developing formulae all have rather large negative temperature coefficients—the development time changing for a 10°C temperature change by a factor of from 1.3 for metol to 2.5 for glycine. Furthermore, unless hardeners are added, developers cannot be used above about 25°C without dangerous softening of the gelatin. Developing formulae are accordingly designed for use at 65–70°F (18–21°C).

For consistent results in photometric work, the solution must be agitated during development to prevent local depletion or variation of the developer strength. Such depletion, if highly localized, may cause a light edge to a dark area (Eberhard effect) or may lead to streaks and irregularities in density. Hand rocking of the tray or, better, brushing is the simplest form of agitation. For large-scale operation, or for situations where great uniformity is desired, several forms of mechanical agitation have been devised.[12]

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[12] Henney and Dudley, *Handbook of Photography*, p. 353. New York: Whittlesey House, 1939.

Various methods are used for the control of development. The simplest method, but one which depends on personal experience and judgment, is that of inspection during development. This method fails for panchromatic or infrared-sensitive emulsions, which must be developed in total darkness, and is, in any case, not suited to exact reproduction of conditions. It is, however, almost essential for the processing of individual spectrographic exposures, where emulsion and source characteristics are not exactly known, and especially in the processing of Schumann plates, where development is often limited by the appearance of background fog.

With the increasingly good control by manufacturers of the activity of developers and of the sensitivity and physical properties of emulsions, the "thermal" system of development has become common, the temperature of the developer and time of development being specified for the emulsion and developer used. Most manufacturers of photographic materials supply time-temperature data for the development of their emulsions. To meet particular requirements, and to take care of individual arrangements of developer agitation, modifications of these recommendations based upon a study of sample test exposures may be found necessary.

Fixing and Hardening. After development, emulsion processing is completed by halting development, hardening, and fixing. These three operations are often carried out in one step in an acid-hardener-fixing bath, after the emulsion has first been rinsed in water. Rinsing removes the superficial developer, and since most developing agents are practically inactive except in alkaline solution, development will stop completely when the alkalinity of the developer left in the gelatin is neutralized.

A separate stop bath (short-stop) is sometimes used to halt development, especially in large-scale work. By this means alkali is kept from the fixing bath, where it might precipitate sulphur in the gelatin with resultant silver sulphide stains. A weak solution of acetic acid, sodium bisulphite, or potassium metabisulphite is commonly used as a separate stop bath, the negatives being immersed in it for a few seconds before fixing.

The alkaline developing solution leaves the gelatin of the emulsion in a soft and fragile state. Hardener is customarily used to prevent emulsion damage through handling. Hardening is especially desirable if the solutions must be used above 70°F, or if the emulsion is to be dried by heating. The hardener may be a separate bath or it may be combined with either the short-stop or the fixer. The most common hardeners are potassium alum, chrome alum, and formalin. Chrome alum is the most expensive, but the most satisfactory if high temperatures (above 100°F) are to be encountered.

After development, any silver halide which was not reduced because of the incomplete development of the latent image, or which was not in the latent image, is still light-sensitive and must be made insensitive or removed if a permanent image is to be ensured. This process, called *fixing*, consists of converting the silver halides to water-soluble silver salts for removal by subsequent washing with water. The almost universally used fixer is sodium thiosulphate ($Na_2S_2O_3$), commonly called "hypo" from its earlier and less correct chemical name, sodium hyposulphite.

Hypo is used in 30 per cent to 40 per cent concentration in a plain fixing bath or, preferably, in a bath made slightly acid to neutralize developer alkali, or, more commonly, where small numbers of negatives are handled, in an acid-hardening-fixing bath, which makes unnecessary the separate short-stop and hardening baths. Sodium sulphite is often added to prevent precipitation of sulphur; ammonium chloride is sometimes added to increase the fixing speed. All manufacturers supply formulae for fixing baths, and ready-mixed fixers are available in powder form.

Fixing should continue at least until the negative is clear and the opalescent silver bromide layer has disappeared. An old rule is that, for safety, the negative should remain in the fixer for a time double this clearing time. Later authorities hold this extra time unnecessary, especially in fresh solutions, and it certainly is not needed if indefinite preservation of the negative is not contemplated.

Washing. Washing is necessary to remove from the gelatin the soluble silver salts formed in fixing and, also, the salts from the fixer bath and traces from the other processing baths. Washing, like development and fixing, is an exponential process, proceeding at a rate which decreases as the amount of soluble material diminishes. The completeness of washing cannot be judged visually; while chemical or electrical tests can be made, a general rule based on experience is to wash for twenty minutes in running water, or for five minutes each in five or six changes of still water. Washing can be hastened by using a spray or sheet of water with such violence as can be withstood by the emulsion, which in that case must be hardened.

Drying. As a result of washing, the emulsion not only carries a layer of surface water but also holds a large amount of water, perhaps ten times its mass, absorbed in the gelatin. Most of the surface water may conveniently be removed with a clean, lint-free blotter, or a moist, viscose sponge. The absorbed water must be removed by evaporation. In dry air at room temperature, drying may take an hour. It can be hastened by circulating the air and by warming it to about 90°F. Bathing the emulsion in alcohol, which replaces the water in the emulsion and evaporates more readily, hastens drying. The most rapid drying of

emulsions, which for this process must have been thoroughly hardened previously, is attained by placing the plates or films over an electric heater while an air blast, which need not be heated, removes the moisture driven out of the emulsion.

Complete processing may consume from one to two hours if no effort is made to attain speed. This time may include two to fifteen minutes for developing, ten to twenty minutes for fixing, twenty to forty minutes for washing, and thirty to sixty minutes for drying, together with a few minutes more for rinsing and handling between the various steps of the process. The time required, however, can be reduced, and at the other extreme may be cited the technique described by Vincent and Sawyer[13] by which contrast plates with thin emulsions have been processed completely in less than three minutes. The steps include development in a hydroquinone-caustic soda developer, hardening in a chrome alum solution, fixing in a hypo-ammonium chloride fixer, washing in a flat stream of water, sponging with a viscose sponge, and drying in an air blast over an electric heater. The approximate time schedule is as follows:

Develop...	30 seconds
Rinse and transfer.................................	10
Harden..	15
Drain and transfer.................................	5
Fix...	25
Drain and transfer.................................	5
Wash..	30
Rinse, distilled water..............................	10
Sponge..	10
Dry...	40
	180 seconds

Plates processed so rapidly might not keep indefinitely in storage. The processing is adequate, however, for many industrial control processes, such as spectrochemical analysis, where reference to the photographic record, after the original measurement, is made within a few days or weeks, if at all.

83. Available Photographic Emulsions

For spectrographic work numerous emulsions are now available and there is a wide choice of speeds, contrasts, and spectral ranges. The silver halides are inherently sensitive to a wide range of wave lengths, extending from a point in the blue-green to the extreme ultraviolet (see page 288). The ultraviolet sensitivity of ordinary emulsions is limited by the absorption of the gelatin, and begins to fall off at about 2500A. Special methods of emulsion preparation and sensitization have, however, extended the range widely in both directions.

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[13] H. B. Vincent and R. A. Sawyer, *Spectrochimica Acta*, I, 131, 1939.

Following the discovery by Vogel, in 1873, that the color sensitivity of emulsions could be extended toward the red by the use of dyes, continuous advance has been made in the use and development of emulsion dying.   Probably the most extensive work has been done at the Research Laboratories of the Eastman Kodak Company under the direction of C. E. K. Mees.   One of the most striking successes of these researches has been the development of the polycarbocyanine dyes—derivatives of quinoline (C_9H_7N) or of benzothiazole ($C_{13}H_7N_3O_4S_2$).   These dyes
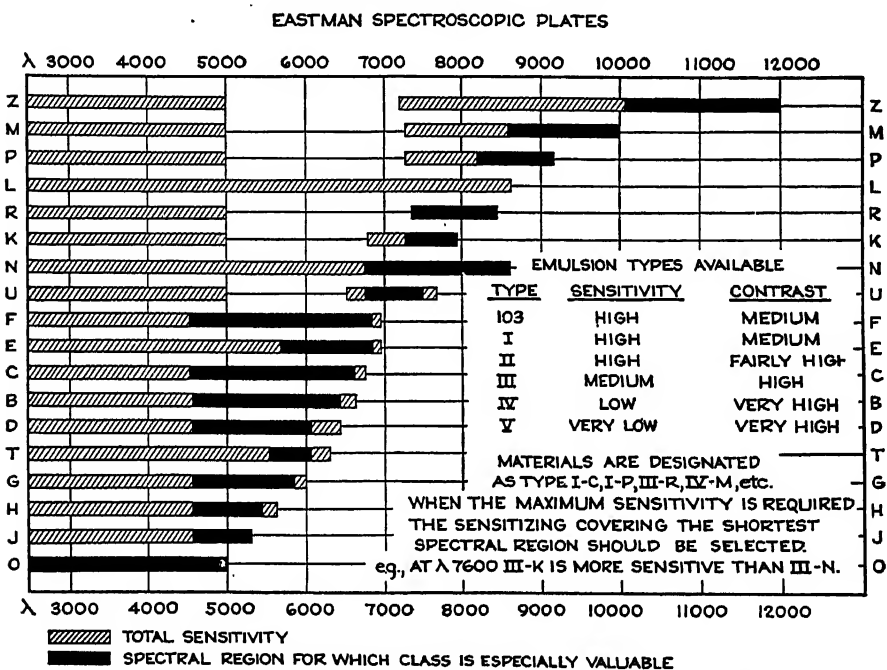
Fig. 78.   Spectral Sensitivity of Selected Color-Sensitized Photographic Emulsions.

consist of two organic groups joined by a chain of carbon and hydrogen atoms (CH groups), with alternate single and double bonds.   The longer the chain of carbon atoms, the further the infrared sensitivity extends.   The dye with the longest chain in this series of compounds (pentacarbocyanine) has eleven carbon atoms and renders emulsions sensitive to somewhat beyond 13,000A.[14]

For use in different regions of the green, red, extreme red, and infrared, the Eastman Kodak Company supplies "Eastman Spectroscopic Plates" with 17 different types of sensitizing.   The ranges of total sensitivity and of highest sensitivity of each of these sensitizings is shown in Fig. 78.

[14] W. Clark, *Photography by Infra-Red*, Ch. V.   New York: John Wiley & Sons, 1939.

Class *O* plates are unsensitized. The other sensitizings cover the whole red region to the present limit near 12,000A. Eastman Spectroscopic plates are supplied with eight different types of emulsions. The characteristics of six of these types are listed in Fig. 78. They will be seen to cover a wide range of sensitivities, contrasts, and graininess. A new emulsion, Type 548, has been added which has very fine granularity and an extreme resolving power of better than 500 lines per millimeter. The eighth emulsion, Type V*a*, is similar to Type V but of somewhat higher speed and coarser grain. Types V and V*a*
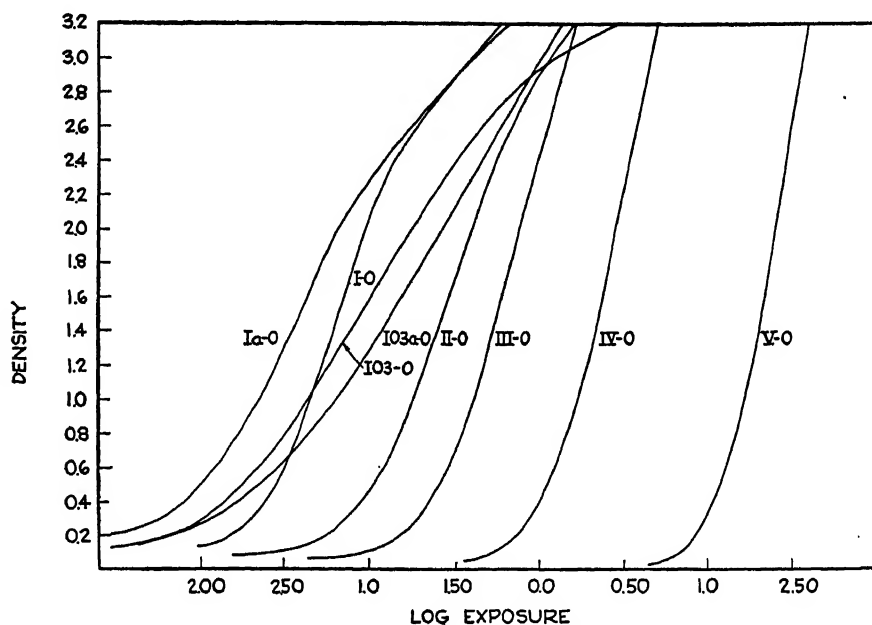
Fig. 79. Characteristic Curves of Kodak Photographic Emulsions.

are too slow for use except with high-aperture instruments and high-intensity light sources. The characteristic curves of most of these emulsions for white light are shown in Fig. 79. Most of the sensitizings can be supplied with any of the emulsions, although a few are offered with only one emulsion. A wide range of plate types are thus available.

Where special sensitizing is not required, various commercial emulsions, made by the Eastman Kodak Company and by other manufacturers, can be used in spectrographic work. Process plates, giving high contrast at low sensitivity, are commonly so used, as well as some orthochromatic and high-speed plates. For metallurgical spectrochemical work, where high contrast, low background, and low or moderate speed are required, and where a thin, hard gelatin must be used to permit

rapid processing, the Eastman Kodak Laboratories have developed a plate similar to the Process plate in many respects and called the "Spectrum Analysis" plate.

Special types of plates are also available for use with ultraviolet radiations of wave lengths shorter than about 2500A. The earliest plates for use in this region were developed by Victor Schumann,[15] who succeeded in producing plates with very little gelatin. The silver halide particles are deposited on the glass mounting with only sufficient gelatin to hold them in place. Plates of this type are still extensively used and have been found to be sensitive down to the shortest optical wave lengths yet recorded—about 15A. Schumann described his technique fully; it has been used and somewhat modified by various workers.[16] Schumann plates are available commercially from Adam Hilger, Ltd., London, England.

It was pointed out by Henri and by Duclaux and Jeantet[17] that ordinary plates can be made sensitive to short wave lengths if they are coated with an oil which fluoresces in ultraviolet light and emits light to which the emulsion is sensitive. Before development of the plate, the oil must be removed with a solvent, such as ether, acetone, or xylene. Various paraffin oils have been used for this purpose, and the properties of several have been investigated by Harrison.[18] Oil sensitizing, while effective to at least 500A, is not very convenient, although the plates thus treated are more uniform in their sensitivity over their entire area than Schumann plates are likely to be, and thus are better for photometric measurements.

The Kodak Research Laboratories have investigated the fluorescence, on exposure to ultraviolet light, of a large number of organic substances. They now provide plates, treated by an undisclosed sensitizer, which at wave lengths longer than 1000A are nearly as sensitive as Schumann plates. These plates are cheaper than Schumann plates and considerably more convenient to use, although the fluorescent material must be washed off with ethylene chloride or cyclohexane before development. The Kodak Laboratories also furnish an Ultra-violet Sensitizing Solution—the ethyl carboxylic ester of dihydrocollidine—with which any plates can be sensitized to the ultraviolet. Fluorescent methods of ultraviolet sensitizing all result in a greater or less loss of resolving power.

In general, it is desirable to use for spectrographic work an emulsion of high contrast, low background fog, and high resolving power. The

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[15] V. Schumann, *Ann. d. Physik*, **5**, 349 (1901); also see Baly, *Spectroscopy*, Vol. II, p. 380.

[16] P. N. Kalia, *Ind. J. Phys.*, **10**, 457 (1936).

[17] V. Henri, *Jour. de Physique*, **2**, 156 (1921); J. Duclaux and P. Jeantet, *Jour. de Physique et le Radium*, **2**, 156 (1921).

[18] G. R. Harrison, *J. Opt. Soc. Am.*, **11**, 113, 1925.

spectral lines then appear sharply against a clear background, and the high contrast permits accurate photometric measurements of small differences in spectral intensities. Plates with these characteristics are generally low in sensitivity; examples are process and contrast plates, and Eastman Types III and IV. Such plates can be used satisfactorily only with spectral sources of high intensity, with spectrographs of high aperture, or under conditions where sufficiently long exposures are possible. Often compromise is found necessary, and contrast and resolving power are sacrificed in order that the sensitivity required by the spectrograph aperture, source intensity, and permissible exposure time may be obtained. However, the use of emulsions of as high contrast and resolving power as are consistent with the other conditions is almost always desirable.

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CHAPTER 9
The Determination of Wave Length

84. Standards of Wave Length

The primary standard of wave length is the wave length of the red cadmium line expressed in terms of the international meter bar. As defined by the action of the International Astronomical Union (see Section 7): "the wave length of the red ray of light from cadmium is 6438.4696 angstroms in dry air at 15°C on the hydrogen thermometer, at a pressure of 760 mm of mercury, the value of g being 980.67 (45°)."[1] This value is based on the measurements by Michelson in 1894, and by Benoit, Fabry, and Perot in 1907. Later determinations of this wave length have differed from the adopted value by not more than one part in three million and usually by much less. It is generally believed that the accuracy of the accepted value is of the order of one part in ten million.

Since, however, the value of the wave length of the red cadmium line is accepted by definition as standard, much more important than its absolute accuracy is the accuracy of the determination of other wave lengths in terms of the primary standard. Direct comparison with the red cadmium line is made by interferometric methods. The process, because of its complexity, is not generally adaptable to the ordinary needs of spectroscopy. The International Astronomical Union has therefore undertaken the establishment of a large number of secondary standards from the spectra of iron and of the noble gases. These secondary standards are to be distributed as regularly as possible throughout the spectrum and are intended to be used for the determination by interpolation of wave lengths in other spectra.

Up to the present, most of the secondary standards are lines in the spectrum of iron, which has been chosen both because of its convenience and because of the large number of lines throughout its whole spectrum. The source for iron lines is "the Pfund arc operated between 110 and 250 volts, with 5 amperes or less, at a length of 12–15 millimeters used over a central zone at right angles to the axis of the arc, not to exceed 1–1.5 millimeters in width, and with an iron rod 6–7 millimeters diameter as the upper pole and a bead of iron oxide as the lower pole." Only such

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[1] For specifications for the operation of the standard cadmium lamp, see *Trans. Int. Ast. Union*, 6, 79, 1938.

TABLE I

IRON SECONDARY STANDARDS

(Adopted by the International Astronomical Union in 1928, 1932, and 1938)

2447.708	3244.190	3727.621	3927.922	4375.932	5123.723
2584.536	3257.594	3732.399	3930.299	4383.547	5127.363
2635.808	3271.002	3733.319	3935.815	4390.954	5150.843
2679.062	3284.588	3734.867	3940.882	4404.752	5167.491
2689.212	3286.755	3737.133	3942.443	4408.419	5168.901
2699.107	3298.133	3738.308	3948.779	4415.125	5171.599
2723.577	3340.566	3748.264	3956.681	4422.570	5198.714
2735.475	3347.927	3749.487	3966.066	4427.312	5202.339
2767.523	3370.786	3758.235	3967.423	4430.618	5216.278
2778.221	3396.978	3760.052	3969.261	4442.343	5227.192
2804.521	3399.336	3763.790	4005.246	4443.197	5242.495
2813.288	3401.521	3765.542	4014.534	4447.722	5250.650
2823.276	3407.461	3767.194	4045.815	4454.383	5270.360
2832.436	3413.135	3787.883	4063.597	4459.121	5307.365
2838.120	3427.121	3790.095	4066.979	4461.654	5328.534
2851.798	3443.878	3795.004	4067.275	4466.554	5341.026
2869.308	3445.151	3797.517	4071.740	4489.741	5371.493
2912.158	3465.863	3798.513	4107.492	4494.568	5397.131
2929.008	3476.704	3799.549	4114.449	4517.530	5405.778
2941.343	3485.342	3805.345	4118.549	4528.619	5429.699
2953.940	3490.575	3815.842	4121.806	4531.152	5434.527
2957.365	3497.843	3824.444	4127.612	4547.851	5446.920
2965.255	3513.820	3825.884	4132.060	4592.655	5455.613
2981.446	3521.264	3827.825	4134.681	4602.944	5497.519
2987.292	3558.518	3834.225	4143.871	4647.437	5501.469
2999.512	3565.381	3839.259	4147.673	4667.459	5506.782
3037.388	3576.760	3840.439	4156.803	4678.852	5569.625
3047.605	3581.195	3841.051	4170.906	4691.414	5572.849
3057.446	3584.663	3843.259	4175.640	4707.281	5586.763
3059.086	3585.320	3846.803	4184.895	4710.286	5615.652
3067.244	3586.114	3849.969	4202.031	4733.596	5624.549
3075.721	3589.107	3850.820	4203.987	4741.533	5658.826
3083.742	3608.861	3856.373	4213.650	4745.806	5662.525
3091.578	3617.788	3859.913	4216.186	4772.817	6027.057
3116.633	3618.769	3865.526	4219.364	4786.810	6065.487
3134.111	3621.463	3867.219	4250.790	4789.654	6136.620
3157.040	3631.464	3872.504	4260.479	4859.748	6137.696
3160.658	3647.844	3873.763	4267.830	4878.218	6191.562
3175.447	3649.508	3878.021	4271.764	4903.317	6230.728
3178.015	3651.469	3878.575	4282.406	4918.999	6252.561
3184.896	3669.523	3886.284	4285.445	4924.776	6265.140
3191.659	3676.314	3887.051	4294.128	4939.690	6318.022
3196.930	3677.630	3888.517	4298.040	4966.096	6335.335
3200.475	3679.915	3895.658	4305.455	4994.133	6393.605
3205.400	3687.458	3899.709	4307.906	5001.871	6421.355
3215.940	3695.054	3902.948	4315.087	5012.071	6430.851
3217.380	3704.463	3906.482	4325.765	5041.759	6494.985
3222.069	3705.567	3907.937	4337.049	5049.825	6546.245
3225.789	3719.935	3917.185	4352.737	5051.636	6592.919
3236.223	3722.564	3920.260	4358.505	5083.342	6663.446
3239.436	3724.380	3922.914	4369.774	5110.414	6677.993

lines are accepted as standards as have been measured concordantly and independently in at least three laboratories, and there are now 306 such iron lines between 6677A and 2447A. Their wave lengths in air, at standard conditions, are given to thousandths of an angstrom unit and are believed to be correct to 0.001A or 0.002A. Table I lists the iron-arc secondary standards of wave length. Preliminary interferometric measurements on other iron lines in the regions 7164A to 10216A and 2101A to 3384A have been published but no lines in these regions except the ultraviolet lines in Table I have as yet been adopted as meeting the requirements for secondary standards.[2]

The International Astronomical Union has also approved, as tertiary standards, the wave lengths of 312 iron lines from 3371A to 6750A, which were obtained by grating or interferometer interpolation.[3] The wave lengths are probably accurate to a few thousandths of an angstrom unit.

It has been found that many neon and krypton lines from discharge tubes are extremely sharp and reproducible. Twenty neon lines in the red and twenty krypton lines in the visible region have been adopted as secondary standards. Their values are given in Table II. These wave lengths are given to eight places and they are probably accurate to about 0.0001A.

TABLE II
NEON SECONDARY STANDARDS
(Adopted by the International Astronomical Union in 1935)

5852.4878	6143.0623	6506.5279
5881.8950	· 6163.5939	6532.8824
5944.8342	6217.2813	6598.9529
5975.5340	6266.4950	6678.2764
6029.9971	6304.7892	6717.0428
6074.3377	6334.4279	7032.4127
6096.1630	6382.9914	

KRYPTON SECONDARY STANDARDS
(Adopted by the International Astronomical Union in 1935)

4273.9700	4362.6423	5570.2895
4282.9683	4376.1220	5649.5628
4286.4873	4399.9670	5870.9158
4300.4877	4453.9179	5993.8503
4318.5525	4463.6902	6421.029
4319.5797	4502.3547	6456.291
4351.3607	5562.2257	

A lack of secondary standards of wave length will be noted in the ultraviolet and infrared regions of the spectrum. This deficiency is likely to be remedied soon in regions where the interferometer can be readily applied. In the extreme ultraviolet region, below 2100A, interferometric methods fail because of the lack of satisfactory optical media

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[2] W. F. Meggers and C. J. Humphreys, *Bur. of Stand. J. of Res.*, **18**, 543, 1937, *Trans. Int. Ast. Union*, 6, 79, 1938.

[3] *Trans. Int. Ast. Union*, 3, 86, 1928.

and of reflecting surfaces. A possibility is offered by the reflection echelon method of Williams,[4] but no one as yet has overcome the considerable technical difficulties in the application of this method in the range of vacuum spectroscopy.[5]

Two other methods have been utilized for the determination of wavelength standards in the extreme ultraviolet, although the results have not so far been verified by enough independent laboratories to lead to their acceptance by the International Astronomical Union. Early attempts to obtain standard wave lengths in the vacuum range were made by the method of the coincidence of overlapping orders of the concave grating. The higher-order spectra of extreme ultraviolet lines were measured by comparison with the first-order lines of iron or copper of wave lengths above about 2300A, which had been measured interferometrically. Wave lengths so determined are subject to the difficulties of the use of overlapping orders first noted in Rowland's standards (Sec. 7); possibly some inconsistencies found in the work of various experimenters may be explained on this basis. Because of the difficulty of introducing comparison spectra in vacuum spectroscopy, most recent attempts at standardization by this method have been concerned not with iron lines but rather with the lines of gaseous elements, such as carbon, oxygen, nitrogen, neon, argon, and mercury, which are apt to be present by accident or design in light sources used in this region, or with the lines of boron, sodium, or silicon often observed when glass discharge tubes are used. An extensive collection of data on such lines, from 1995A to 105A, has been published by Boyce and Robinson.[6] The wave lengths are given in different cases to one, two, or three decimal places. Since the values are collected from the work of different laboratories, they may not be entirely consistent, and, as the authors point out, cannot be used indiscriminately as standards. Weber and Watson[7] have published to three decimal places wave lengths obtained by the coincidence method for 40 lines of carbon, nitrogen, and oxygen between 1931A and 1084A, and have compared them with similar measurements on the same lines by Boyce and Rieke.[8] The mean deviation of the two sets of values is .009A and is believed by the authors to be largely due to the accidental errors of measurement.

The second method of determination of extreme ultraviolet standards is direct calculation from series formulae or from term differences based on interferometrically determined, longer wave-length lines. Thus,

[4] W. E. Williams, *Proc. Phys. Soc.*, **45**, 699, 1933.

[5] Some preliminary experiments but no results have been reported by D. L. MacAdam, *Phys. Rev.*, **50**, 185, 1936.

[6] J. C. Boyce and H. A. Robinson, *J. Opt. Soc. Am.*, **26**, 133, 1936.

[7] R. L. Weber and W. W. Watson, *J. Opt. Soc. Am.*, **26**, 307, 1936.

[8] J. C. Boyce and C. A. Rieke, *Phys. Rev.*, **47**, 653, 1935.

Paschen[9] and Penney[10] have calculated the wave lengths of several extreme ultraviolet lines of hydrogen and of ionized helium from the series formulae, with the aid of values for the Rydberg constants obtained by interferometric measurements on longer wave-length lines of these spectra.   The two sets of values agree to about .001A.

An instance of the calculation of wave lengths from term values is the work of Shenstone[11] on Cu II.   As a result of his exhaustive study, in which very accurate term values were obtained from grating and interferometer measurements of this spectrum throughout the whole photographic region, he was able to calculate the wave lengths of more than 150 lines between 2000A and 685A.   The accuracy is believed to be 0.1 cm^{-1}, which corresponds to an error varying from .003A at 1700A to .0006A at 800A.   By interpolation, More and Rieke[12] have used these copper lines as standards for the direct determination of the wave lengths of 50 lines of carbon, oxygen, and nitrogen in this region.   By making a weighted average of their results together with those of Boyce and Rieke and of Weber and Watson, they have arrived at mean values for 31 of these lines between 1658A and 832A which they believe to be accurate to a few thousandths of an angstrom unit.

As a consequence of an extensive study of the ultraviolet spectra of Fe I, Fe II, and Fe III, in which he identified many new terms and classified a large number of lines, Green[13] has been able to calculate the wave lengths of many ultraviolet iron lines.   Of these, 17 Fe I lines between 1862A and 2106A, and 81 Fe II lines between 1550A and 2221A are regarded as especially suitable as standards.   The term values of a few other elements are well enough known to permit the calculation from them of the wave lengths of extreme ultraviolet lines of their spectra.   There is every reason to believe that the analysis of other elements will be brought to the necessary stage of refinement.   Until the use of the reflection echelon in the extreme ultraviolet is perfected, this method for obtaining ultraviolet standards of wave length seems the most promising.   At present, the spectroscopist in this field must choose his standards of wave length with care and discrimination.   Especially if the dispersion of his equipment is such as to justify measurement to better than .01A, difficulty may be experienced in selecting a set of standards which is self-consistent throughout the whole vacuum region.

A principal source of uncertainty in the determination of wave-length standards in the extreme ultraviolet is the fact that the primary standard

[9] F. Paschen, *Preuss. Akad.*, p. 662, 1929; also Boyce and Robinson, *loc. cit.*

[10] W. G. Penney, *Phil. Mag.*, **9**, 661, 1930.

[11] A. G. Shenstone, *Phil. Trans.*, **235A**, 195, 1936.

[12] K. R. More and C. A. Rieke, *Phys. Rev.*, **50**, 1054, 1936.

[13] L. C. Green, *Phys. Rev.*, **55**, 1209, 1939.   Note: Most of the wave lengths in this and the preceding four references are reprinted in the article "Spectroscopy in the Vacuum Ultraviolet," by J. C. Boyce, *Rev. Mod. Physics*, **13**, 34, 1941.

and the secondary standards are given as wave lengths in air under normal conditions. By means of the refractive indices for air at the corresponding wave lengths, these values must be converted to vacuum wave lengths for comparison by the coincidence method ($\lambda_{vac} = \lambda_{air} \cdot n$) and to wave numbers in vacuum for the calculation of terms. These conversions have been based on the determination of the refraction of air by Meggers and Peters.[14] Within the last few years, several observers have published data on the dispersion of air which indicate slight errors in the values of Meggers and Peters. Table III tabulates some of these results. The results of Meggers and Peters appear to be too large at

TABLE III

REFRACTIVITY OF DRY AIR AT 15°C AND 760 MM, $(n - 1)10^7$

λ	Meggers and Peters	Sears	Kösters and Lampe	Perard
2000	3255.8	3190.6	3216.7	3264.7
3000	2906.9	2912.6	2916.4	2920.5
4000	2817.1	2826.8	2828.0	2827.2
5000	2781.3	2789.2	2790.0	2788.8
6000	2763.3	2769.2	2770.1	2769.3
7000	2753.0	2757.4	2758.4	2758.0
8000	2746.5	2749.8	2750.9	2750.7
9000	2742.1	2744.6	2745.8	2745.8
10000	2739.1	2740.9	2742.2	2742.4

2000A and too small above about 2500A. For example, Sears' values lead to a vacuum wave length of the primary standard of $\lambda_{vac} = 6440.2498A$, while Meggers and Peters' data give $\lambda_{vac} = 6440.2453A$—a discrepancy larger than the experimental error. A further difficulty is the fact that the relative values of the vacuum wave lengths of the secondary standards will be affected by the choice of dispersion data, since the various sets of figures do not have a constant relative value. The International Astronomical Union hopes to have enough data available soon to fix new standards for the dispersion of air.

As indicated earlier, the present secondary iron standards of wave length are probably accurate to .001A or .002A. The limitations are due to slight uncertainties in the corrections for temperature, humidity, and CO_2 content of the laboratory air, to lack of agreement between different observers as to the correction for the phase change at the reflections from the metallic reflecting surfaces of the etalons, and primarily, probably, to the width of the lines emitted by the Pfund arc in air. Williams' application of the reflection echelon to wave-length determination permits the direct determination of vacuum values and also avoids the difficulty with metallic reflections. Using as a light source a discharge in an iron hollow cathode, Williams and Middleton[15] have found

[14] W. F. Meggers and C. G. Peters, *Bull. Bur. of Stand.*, **14**, 687, 1918.
[15] W. E. Williams and A. Middleton, *Proc. Roy. Soc.*, **172A**, 159, 1939.

that the lines are narrow enough to permit determination of vacuum wave lengths with an uncertainty of .0001A or .0002A.

The 47 wave lengths which they obtained are given in Table IV, together with the wave lengths in normal air calculated from the dispersion data of Kösters and Lampe. Except for the twelfth line and the last line, which are not secondary standards, the accepted standard value is also given corrected to a vacuum arc by means of Babcock's equation for term depression due to pressure. It will be noted that the

TABLE IV

IRON VACUUM WAVE LENGTHS DETERMINED BY REFLECTION ECHELON

Vacuum Wave Length	Calculated Normal Air Wave Length	Previous Value of Air-Arc Wave Length Corrected for Pressure	Vacuum Wave Length	Calculated Normal Air Wave Length	Previous Value of Air-Arc Wave Length Corrected for Pressure
5372·9847	5371·490$_5$	0·491 S	3816·9226	3815·839$_1$	0·840 S
5228·6435	5227·188$_0$	{ 0·189 / 0·188 S }	3791·1669	3790·090$_1$	0·093 S
5173·0379	5171·597$_0$	0·596 S	3788·9542	3787·878$_0$	0·881 S
5168·9276	5167·487$_7$	0·488 S	3759·2998	3758·231$_3$	0·233 S
4529·8844	4528·614$_1$	0·615 S	3738·1939	3737·130$_9$	0·132 S
4428·5511	4427·307$_5$	{ 0·311 / 0·306$_5$ S }	3735·9247	3734·862$_2$	0·865 S
4416·3620	4415·121$_6$	0·122 S	3728·6780	3727·617$_4$	0·619 S
4405·9868	4404·749$_2$	0·749 S	3720·9915	3719·932$_9$	0·934 S
4377·1597	4375·929$_7$	0·931 S	3688·5040	3687·453$_8$	0·456 S
4326·9786	4325·761$_8$	{ 0·764 / 0·761$_5$ S }	3680·9599	3679·911$_7$	0·914 S
4133·2220	4132·056$_0$	0·058 S	3648·8813	3647·841$_3$	0·842 S
4064·7410	4063·592$_9$	0·594	3632·4969	3631·461$_2$	0·462 S
3931·4089	3930·295$_6$	0·298 S	3619·7988	3618·766$_4$	0·767 S
3929·0309	3927·918$_3$	0·921 S	3609·8880	3608·858$_1$	0·859 S
3924·0214	3922·910$_1$	0·913 S	3566·3965	3565·377$_8$	0·379 S
3921·3670	3920·256$_4$	0·259 S	3522·2674	3521·260$_1$	0·262 S
3861·0042	3859·909$_3$	0·912 S	3514·8212	3513·815$_8$	0·818 S
3857·4626	3856·368$_6$	0·372 S	3498·8397	3497·838$_4$	{ 0·843 S / 0·840$_6$ }
3842·1354	3841·045$_4$	0·048$_5$ S	3477·6962	3476·700$_3$	{ 0·704 S / 0·702$_3$ }
3841·5250	3840·435$_2$	0·437 S	3466·8523	3465·859$_2$	{ 0·862 S / 0·861$_0$ }
3835·3084	3834·220$_2$	0·223 S	3414·1091	3413·129$_5$	{ 0·131 S / 0·130$_6$ }
3828·9069	3827·820$_3$	0·822$_5$ S	3408·4355	3407·457$_3$	{ 0·459 S / 0·457$_9$ }
3826·9650	3825·878$_9$	0·882 S	3287·6982	3286·750$_8$	{ 0·752 / 0·750$_7$ }
3825·5271	3824·441$_4$	0·443 S			

The lowered final figures are doubtful. In the third and sixth columns, the integral part of the wave length is replaced by 0.
S indicates secondary standard lines.

new and previous values differ by amounts which in one case are as large as .004A.

While the present secondary standards are satisfactory for most needs, it is probable that further developments in spectrographic dispersion and resolving power will eventually necessitate the adoption of the more accurate vacuum lengths from low-pressure sources.

85. Spectroscopic Charts and Tables

For orientation purposes and for rapid identification of spectra, it is desirable to have charts or standard spectrograms, at least of the more common spectra. Since the iron spectrum is often used as a reference standard, charts or identified spectrograms of iron are almost indispensable. It is more convenient if these charts are made with the same spectrograph, and hence with the same dispersion, as the spectra with which they are to be compared. In any case, it is much simpler to compare prism spectra with prism spectra and grating with grating. If the dispersions of the spectra under comparison are not the same, a simple system can often be arranged to project one onto the other with magnification to match the dispersions.

Numerous spectrum charts and atlases are available. The following are among the most important:

1. Hilger charts (A. Hilger, London). Enlarged photographs, on cards, of the discharge tube spectra of neon from 7032A to 5852A and of helium from 7281A to 3613A, and of the arc spectra of iron from 10216A to 2084A and of copper from 5782A to 2043A. The spectra are taken with a large quartz spectrograph. Nearly every wave length is marked. A portion of one of the iron charts is shown in Fig. 80.

2. *Atlas typischer Spektren*, J. M. Eder and E. Valenta, (Hölder: Vienna 1911, reprinted 1928). The old classic atlas of 70 elements in the range 7000A–1850A, with over 600 photographs of flame, arc, and spark spectra taken with glass and quartz prism spectrographs and with small grating spectrographs. Many of the stronger lines are identified. Wave lengths are given on the Rowland scale. This atlas is very useful for rapid orientation.

3. *Atlas der Restlinien*, A. Gatterer and J. Junkes (Specola Vaticana, Castel Gandolfo, Italy, 1937). Twenty-eight photographs of the spectra of 30 elements in the range 8000A–2200A. Prism spectra of pure elements taken with a juxtaposed iron spectrum. Three exposure times for each element. Dispersion from 12 A/m at 8000A to 1.1 A/m at 2200A.

Another type of atlas, useful for qualitative spectrochemical analysis, shows the most sensitive or residual lines of the elements with a juxtaposed iron spectrum. With the aid of such an atlas, qualitative analysis

Courtesy of Adam Hilger, Ltd.

Fig. 80.   Portion of Reference Chart of the Arc Spectrum of Iron.

can often be performed without the measurement of any wave lengths. Atlases of this type are:

1. *Atlas de Spectre d'Arc*, J. Bardet (Doin, Paris, 1926). Fifty-four charts of an enlargement of the arc spectrum of iron taken with a quartz spectrograph in the region 3570A–2500A. The whole region extends over eight charts, and each of six series of these eight charts shows the iron spectrum and, beside it, the position and intensity of many lines of the arc spectra of several elements. Thirty elements are included in the whole set.

2. *Metallurgical Spectrum Analysis*, W. S. Crook (Stanford University Press, 1935). Twenty charts of an enlargement of the iron arc spectrum in the regions 3428A–2796A and 5670A–5056A, taken with a 21-foot grating. The dispersion is about 5 mm per angstrom. The positions of many of the arc lines of 21 elements are marked beside the enlargement, with an indication of relative intensity.

3. *Atlas der Letzten Linien der Wichtigsten Elemente*, F. Löwe (Steinkopf, Dresden, 1928). Charts taken with a small quartz spectrograph in the region 4700A–2200A, for 43 elements. The spark spectra are shown for solutions in concentration of 1, .1, .01, and .001 on graphite electrodes. Thus, only the more persistent lines are shown, together with the effect on them of concentration.

4. *Chemical Spectroscopy*, W. R. Brode (Wiley, New York, 1939). Contains an enlarged arc spectrum of iron extending from 5081A to 2310A taken with a large prism spectrograph on 35 plates. Nearly all the lines are identified by wave length, and, beside the spectra, the position is indicated of several hundred of the principal lines of most of the elements.

In addition to charts for the identification of the principal lines of any spectrum, it is desirable to have at hand compilations of the wave lengths of the lines emitted by the various atoms in different stages of excitation and ionization. The number of lines which can be emitted by each atom in any of its possible stages of ionization is actually infinite. Practically, the number which are excited by ordinary sources and are resolvable or detectable by usual methods is finite, though large. Millions of lines are probably measurable if all 88 known atoms are considered; tens of thousands have been measured and recorded.

Although determinations of spectroscopic wave lengths are among the most precise physical measurements, and although relative intensity measurements can be made with considerable ease and accuracy, at present but few spectra have been completely and carefully studied. The available data have been produced by a large number of investigators and laboratories and are widely scattered through the periodical literature.

An attempt at an inclusive collection of spectrographic data was made by H. Kayser in Volumes 5 and 6 of his monumental *Handbuch der Spectroscopie*. A complete bibliography and critical history of the spectrum of each element was accompanied by a compilation of all wave lengths observed by the principal investigators. Volume 5, covering 45 elements from Argon to Nitrogen, appeared in 1910, and Volume 6, covering 41 elements from Sodium to Zirconium, in 1912. These volumes appeared just as the inadequacies of the Rowland system of wave lengths were being recognized and the change to the international angstrom system of wave lengths was being made. Furthermore, just at this time the appearance of the Bohr theory stimulated a new interest and productivity in spectroscopic research.

Subsequently, Kayser initiated in his own laboratory a program of remeasurement of the arc and spark spectra of all the elements in international units and began the preparation of a revision of Volumes 5 and 6 of his *Handbuch*. The work was interrupted by the First World War. The task was rendered almost insuperable by the flood of publications in the field in the years immediately after the war (page 15). In 1924 H. Kayser and H. Konen published Volume 7, Part 1, of the *Handbuch*, containing new data on air and on 20 elements from A to Fe (Argon to Iron), and in 1930, Volume 7, Part 2, containing data on 10 elements from Ga to Ir (Gallium to Iridium). So much new data on the earlier elements had accumulated in the meantime that Volume 8, which appeared in 1932, covered only new material on 19 elements from Ag to Cu (Silver to Copper), and yet included nearly as many pages as Volume 7, Parts 1 and 2 (654 pages against 750). A large part of the increase in size was due to the attempt to include data on the classification of atomic spectra of various stages of ionization and on the associated band spectra. The third and final part of Volume 7, appearing in 1934, contained 723 pages and covered 14 elements from Il to Nb (Illinium to Columbium) as completely as was done for the elements in Volume 8. It appears unlikely that further revision and publication of the *Handbuch* will be possible. For about half the elements, therefore, no systematic collection of wave lengths pertaining to each element has been published since 1912.

A large amount of spectroscopic data has been published in the *Tables Annuelles de Constantes et Données Numériques* (University of Chicago Press, Chicago, and McGraw-Hill, New York), Volumes I–X, 1912–1934. Both emission and absorption spectra of atoms and of molecules are covered. A large amount of data, including wave lengths, energy levels, and classifications, is given, together with references to the literature through 1930 (Vol. X). In general, the arrangement is chronological by volumes, and hence not very convenient for rapid use.

For data and for information on the present status of the spectra of any of the elements, and especially of those with chemical symbols beginning with letters in the latter half of the alphabet, reference must be made to the abstract journals, such as *Science Abstracts* (*A*) or *Physikalische Berichte*, and to the various spectroscopic bibliographies. The most complete bibliography of the literature up through 1931 is that of R. C. Gibbs in the *Reviews of Modern Physics*.[16] A bibliography, chiefly of the classified spectral lines of neutral and ionized atoms, accompanies the discussion of each spectrum in *Atomic Energy Levels*, by R. F. Bacher and S. A. Goudsmit (McGraw-Hill Book Co., New York, 1932). Many references to published measurements of atomic spectra are given in the *M.I.T. Wave-length Tables*, G. R. Harrison, ed. (John Wiley and Sons, New York, 1939).

There are numerous more or less abbreviated tables of atomic wave length which are valuable and useful within the limits of the material covered. These tables are of two types: (*a*) listings by elements or by order of wave length of the ultimate persistent or sensitive lines of the elements; (*b*) listings by elements or by order of wave length of the principal lines of the elements.

In the first type usually from two to ten lines are given for each element, with a total of from 350 to 1000 lines. These lists are useful in qualitative analysis or in preliminary checking for the presence of suspected impurities. For final decision it is usually necessary to have more complete tables of the lines of elements in question. Abbreviated tables are given in:

1. *Chemical Spectroscopy*, W. R. Brode (Wiley, New York, 1939). Contains (*a*) table of persistent lines, arranged by wave length, giving 400 lines for 71 elements from 9000A to 1600A; (*b*) table of the same lines by elements.

2. *Handbook of Physics and Chemistry*, 27th ed. (Chemical Rubber Publishing Co., Cleveland, 1943). Contains (*a*) table of 470 persistent lines, arranged by wave length, of 82 elements from 9238A to 303A; (*b*) table of the same lines by elements.

3. *M.I.T. Wave-length Tables*, G. R. Harrison, ed. (Wiley, New York, 1939). Contains (*a*) table of 500 sensitive lines of 85 elements from 9237A to 2025A arranged by wave length; (*b*) table of the same lines by elements.

4. *Wave Length Tables for Spectrum Analysis*, F. Twyman and D. M. Smith (Hilger, London, 2nd ed., 1931). Contains (*a*) a list of standard wave lengths; (*b*) a list of the distinctive spark lines determined by Hartley and his co-workers for 42 elements, about 1300 lines arranged by elements from 6708A to 2082A; (*c*) a list of sensitive and ultimate lines

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[16] R. C. Gibbs, *Reviews of Modern Physics*, **4**, 278, 1932.

in spark spectra determined by de Gramont for 83 elements, 330 lines from 7948A to 2138A arranged both by elements and in order of wave lengths; (d) a list of the sensitive arc lines of 50 elements found in R. U. powder,[17] 367 lines from 6708A to 2288A; (e) a list of sensitive lines in flame spectra for 25 elements, 98 lines from 7699A to 2284A arranged both by elements and in order of wave lengths.

The extent of any list of the principal lines of the elements is arbitrary and is fixed only by the choice of the weakest lines to be included. The most important and extensive publications of lines listed by elements are those, already mentioned, in various volumes of the *Tables Annuelles de Constantes et Données Numériques* and of the Volumes 5, 6, 7, and 8 of the *Handbuch der Spectroscopie*. Each of these publications contains about 150,000 lines (with some duplications).

There are two important tables of principal lines given in order of wave length:

1. *Tabelle der Hauptlinien der Linienspektren aller Elemente*, H. Kayser and R. Ritschl (Springer, Berlin, 1939). Contains about 27,000 lines in the range from 90850A to 33A for 88 elements in arc, spark, and Geissler discharges.

2. *M.I.T. Wave-length Tables*, G. R. Harrison, ed. (Wiley, New York, 1939). Contains 109,275 lines in the range from 10,000A to 2000A for 87 elements in arc, spark, and discharge tubes. Since about three-fourths of the wave-length values are based on new grating measurements at the Massachusetts Institute of Technology, this collection presents the most consistent and accurate available collection of wave lengths. It is also reasonably complete. Iron lines in the number 4757 are given, together with a similar number for other atoms having many lines. This table is indispensable for spectrochemical work and for identification of impurity lines or other lines of unknown origin.

In general, collections of data on the band spectra of molecules are not so complete nor so detailed as those on line spectra. Volume 6 of Kayser's *Handbuch der Spectroscopie* contains a table of about 2600 band heads arranged in order of wave length from 7497A to 2046A, together with an indication of their probable source and the direction in which they are degraded. Many new bands have been discovered since the publication of this table, and the assigned origin of some has been changed. The *M.I.T. Wave-length Tables* list, along with the lines, 1381 of the more common band heads. A very useful reference on band spectra is:

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[17] R. U. powder, sold by Adam Hilger, Ltd., was developed for spectroscopic purposes in the laboratories of the British General Electric Co., and contains 50 elements in traces such that when it is burned in an arc only the most persistent lines of each appear.

The Identification of Molecular Spectra, R. W. B. Pearse and A. G. Gaydon (Chapman and Hall, Ltd., London, 1941). Contains (*a*) a table, in order of wave length, of 1653 persistent band heads between 10,600A and 2006A; (*b*) a description of the band systems of many. individual compounds; (*c*) 42 illustrative plates of important band systems; (*d*) a list of persistent atomic lines; and (*e*) hints on the identification of band systems.

For detailed information on the fine structure of a band or on the complete band system of a molecule, it is generally necessary to consult the original periodical literature, although some of this information is to be found, for the molecules there discussed, in Volume 8 of Kayser's *Handbuch* and in the various volumes of the *Données Numériques*. Bibliographical references and vibrational and rotational constants for molecular spectra are given in the following books:

1. *Molecular Spectra and Molecular Structure: I, Diatomic Molecules*, G. Herzberg (Prentice-Hall, New York, 1939). Contains data on all known diatomic molecular spectra, 255 in all.

2. *Report of Band Spectra of Diatomic Molecules*, W. Jevons (University Press, Cambridge, 1932). Contains data on the bands of 142 diatomic molecules.

3. *Molekulspektren, Vol. I, Tabellen*, H. Sponer (Springer, Berlin, 1935). Contains data on the bands of about 150 diatomic molecules and of about 220 polyatomic molecules.

86. Comparators and Measuring Microscopes

For the reduction of spectrograms where any but the roughest accuracy is required, the position of the lines on the plate must be measured as exactly as possible. For these measurements some form of comparator with a least count of about .001 mm is used. Such instruments are offered by various manufacturers and fall into three general classes, as follows:

1. The plate and an excellent scale, usually ruled on glass, are mounted on a carriage which moves on ways under a fixed microscope. A clamping mechanism and a slow-motion screw permit any spectral line to be set under the microscope cross hairs. The line position is then read from the scale by a second fixed microscope or by a projection on a screen. A much rarer variant has the plate carriage fixed, and the two microscopes move as a unit.

2. The plate is mounted on a fixed carriage and a microscope travels over it on ways. A nut under the microscope mounting is driven by an accurate screw. When the microscope is set on a spectral line, a scale beside the microscope mount gives its position in terms of the pitch of

the screw, usually 0.5 mm or 1.0 mm, while a divided head on the screw gives the fraction of a turn of the screw.

3. This type is the exact inverse of the second: the microscope is fixed, while the plate on its carriage is driven by the screw.[18]

An example of the first class of instrument is the Abbe comparator manufactured by Carl Zeiss, Inc. In this instrument the measuring scale is read by the reading microscope which carries in its eyepiece a unique spiral micrometer with a least count of .001 mm. A Spiral of Archimedes, engraved on a glass plate, can be rotated about an axis outside the field of view until one turn of the spiral coincides with one of the scale marks. The turn number and fraction of a turn are read on scales in the field of view, and hence without the necessity of removing the eye from the eyepiece to read an external micrometer drum. The glass measuring scale is 100 mm long in a small model and 200 mm long in a larger. The observing microscope is rigidly attached to the reading microscope by a cross member which has approximately the same coefficient of expansion as the glass scale. Temperature effects in the instrument are thus practically eliminated.

This type of instrument, depending on a glass scale rigidly attached to the plate carriage, has certain definite advantages. With a good dividing machine, it is somewhat easier to produce an accurate glass scale than it is to cut and grind an equally good screw and nut so that they run accurately together. The glass scale is not subject to wear, which might affect the accuracy of the screw, nor does it need the care, cleaning, and oiling which the screw demands. Furthermore, it is free from the erratic errors which may appear in the screw because of backlash, or because of variation, caused by temperature fluctuations and dirt, in the thickness and uniformity of the oil film between the nut and screw.

A serious drawback to these instruments is the fact that the least count of the glass scales is ordinarily 0.1 mm. Small intervals are determined by setting and reading a micrometer eyepiece in the scale-reading microscope, or by reading a vernier on a projected scale. Although the Zeiss instrument attains by this means a least count of .001 mm, most observers find the use and setting of a second microscope tiring and time-consuming if many lines are to be read.

An example of the types of instruments which use a screw as a means of measurement is shown in Fig. 81. It is a large, moving-carriage instrument built by the Gaertner Scientific Corporation. Plates of any

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[18] T. N. Whitehead, *The Design and Use of Instruments and Accurate Mechanism*, Ch. XI, New York: The Macmillan Company, 1934, gives an excellent discussion of the design problems and of the desirable characteristics of measuring microscopes; also of the systematic errors of one design, pp. 14–31.

length can be mounted on the stage, which accommodates directly plates up to 50 cm long and 10 cm wide. The actual travel of the carriage is 20 cm, and the stage slides on the carriage so that the whole 50-cm length can be measured without moving the plate. The screw has a pitch of 1 mm, the micrometer drum has 1000 divisions, and so the least count is .001 mm, while fractions of this unit can be estimated. An interesting
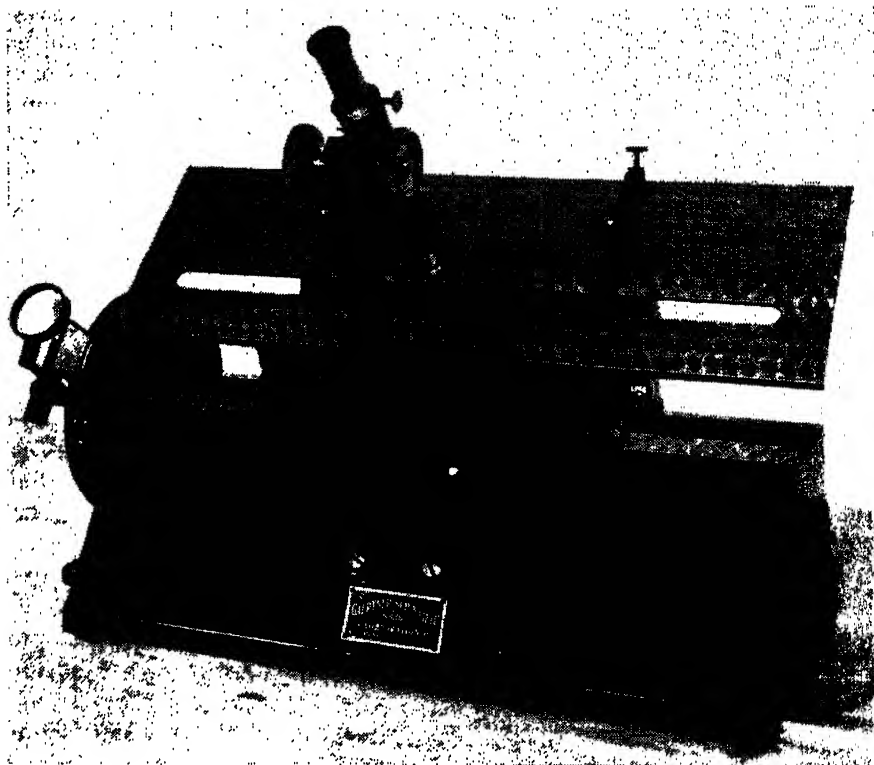
Courtesy of the Gaertner Scientific Corporation.

Fig. 81. Moving-Carriage Comparator.

feature is the placing of the handle for the screw at the left end, thus leaving the right hand free for recording measurements.

If a large number of spectral lines are to be measured, the process of setting the microscope on each line, reading the scales, and recording by hand is fatiguing and relatively slow. G. R. Harrison,[19] on the basis of experience with a very extensive spectrum-measuring program, has reported that an average student assistant may be expected to handle about 60 lines per hour over a seven-hour day, while an experienced operator may perhaps triple this output. Various devices have been

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[19] G. R. Harrison, *J. Opt. Soc. Am.*, **25**, 169, 1935.

developed to lessen the labor and shorten the time required.   Kayser[20] designed an attachment to his screw-type comparator by means of which the operator, by pressing keys, can print on a strip of paper both the exact screw setting and an estimate of the line intensity.   The time required for measurement is estimated to be less than half that with hand recording, but the vibration of printing tends to cause the plate to shift and so destroy the accuracy.

A further improvement, ascribed by Harrison (*loc. cit.*) to M. Sieg-bahn, is that of projecting an image of the spectrum on a screen in front of the operator, thus eliminating the tiring observation through a micro-scope.   This projection is possible only on a fixed-microscope instrument. It is usually best to place a mirror overhead and reflect the projection back on a screen, which may be a sheet of white paper on the table in front of the comparator.   Any kind of fiducial mark for setting can be drawn on this screen.   A microscope objective of low power may be used for the projection, and in that case the microscope eyepiece is removed.

It is somewhat better, however, to use a good anastigmatic camera lens, such as an f/3.5 Tessar lens of about three-inch focal length.   An image with a magnification of ten diameters will be formed at approxi-mately 30 inches from such a lens, which places the reflecting mirror just above the operator's head.   It has been found at the University of Michigan that the projected image with a Tessar lens sacrifices none of the detail that can be seen with a low-power microscope.   A more powerful illumination system will be required, however, than is used for direct microscope observation.   For this purpose the condensing system of a small projection lantern can be arranged with a 100- or 250-watt bulb to focus in the projecting lens a beam which has been reflected at the illuminating mirror of the comparator.   A water cell may be needed in the condensing-lens system to avoid too much heat; otherwise, a long time might be required for the system to reach thermal equilibrium.

A projection comparator has been used by Harrison[21] as the basis for a remarkable instrument which, for grating spectrograms, provides automatic measurement, reduction, and recording of wave length and a microphotometer trace of line intensities.   The original paper should be consulted for the details of this machine, since only the principal features can be noted here.   The basic machine is a 60-cm moving-plate com-parator arranged to project the spectrum on the slit of a microphotometer with a powerful a-c amplifier.   The motor-driven comparator screw is geared to the reducing machine, the gears of which can be arranged to

[20] H. Kayser, *Handbuch der Spektroscopie*, Vol. I, p. 644.
    [21] G. R. Harrison, *J. Opt. Soc. Am.*, **25**, 169, 1935 and *Rev. Sci. Inst.*, **9**, 15, 1938; G. R. Harrison and J. P. Molnar, *J. Opt. Soc. Am.*, **30**, 343, 1940.

give on its dials direct readings of wave length for any grating. The microphotometer trace is recorded directly on a 35-mm film, and on the same film are photographed the dial readings at the instant the trace reaches each line maximum. This machine can record wave lengths of as many as 4000 lines on a 20-inch spectrum plate in two minutes, with an accuracy considerably better than that of hand setting.

87. Notes on the Use and Testing of Comparators

Several forms of cross-hair or fiducial line are in use in comparators. The most common are: (a) a single vertical line; (b) a vertical and a horizontal line (at right angles); (c) two closely spaced vertical lines; (d) two inclined lines, usually at an angle of 60° to one another. The particular form used is largely a matter of individual preference, although a few general considerations may be mentioned.

The single vertical cross hair is probably most often used as a graticule line in spectral-line measurement. It should be considerably narrower than the spectral-line image on which a setting is to be made. The attempt is made to set the line at the center of the line area, or at the densest part of the line. If the line is symmetrical, these two positions are identical; otherwise personal judgment is involved. In either case, a fine cross hair is helpful.

A second hair at right angles to the vertical hair is useful in adjusting the plate so that the relative motion of microscope and plate is at right angles to the spectral lines. It is also valuable in assuring that the lines are all measured at the same place along their length and thus preventing any error from line curvature.

A variant of the single line is a half-line—a single line extending half the length of the spectral-line image. Its users feel that the center of the line can be more easily located if the line appearance at the end, as well as on each side, of the cross hair can be seen. Such a half-line can be produced by mounting a fine glass or quartz pointer in the eyepiece, or, in the projection type of comparator, by drawing a suitable line on the screen. A form of line, similar in principle to a half-line, is a broken or dotted line.

Two parallel vertical lines are most useful if their separation is such that the line to be measured appears encompassed between them. Accordingly, this arrangement is best when all lines have nearly the same width, as they do in the case of scale marks. In most spectra, the apparent line width varies greatly with line intensity, and the chief advantage of two cross hairs is lost, since they must either be too widely separated for accurate setting on fine lines, or so close that they do not span, but partly obscure, the edges of wide lines.

The use of a vertical hair which is set on a line depends for best results on sufficient transmission of light through the spectral lines so

that the cross hair can be seen against the line image or appears imbedded in it.   Settings are very difficult if the spectral line is so dense that the cross hair disappears in it.   This difficulty arises especially with Schumann plates, for the extremely thin emulsion of these plates results in a very closely packed and opaque silver deposit in the line images.   For such very opaque lines it is usually better to use two inclined cross hairs, preferably at an angle to one another smaller than 90°—perhaps 50° or 60°.   Some observers prefer this X-arrangement for all lines. It suffers, however, from the great disadvantage that only a very short length of line is utilized, and any imperfections, scratches, or dust particles in this length form a serious handicap to accurate setting.

For the measurement of spectral lines, it is best to make more than one setting on each line.   There is fairly general agreement, however, that, except possibly for beginners, it is hardly worth while to make more than two or three settings, averaging them mentally if they agree satisfactorily, and recording the mean.   If more readings are made, it is usually found that the eye has unconsciously selected some characteristic or irregularity of the line, and settings are made on that rather than on a new judgment of the line center.

Most observers will be found to have a personal or systematic error in their judgment of line center, one observer setting consistently to the right or left of another.   Since relative position only of the lines is ordinarily desired, this personal factor introduces no trouble, if all lines are of the same character, except in cases of extremely rapid variation of dispersion.   With variations in line width, intensity, and form, however, such a systematic set will introduce errors in the determination of the relative positions of lines of different character.   The difficulty can be largely eliminated if the plate is turned end for end and read again, beginning at the end opposite to that from which the first set of measurements was read.   The systematic error should then work to make too large distances which were first read too small, and a mean of the two sets of readings should show little of the effect.   The labor of reading plates, of course, is thereby doubled.   Before adopting the procedure of reversal, it is well for an observer to determine by a study of his results on the reduction of a known spectrum, with lines of widely varying character, whether his systematic error of setting justifies this additional effort.

Measuring microscopes should be provided with a range of magnifications roughly from about 5 to 25 powers.   This range is most easily provided by using two or three eyepieces of different powers with one or two objectives, and a variable tube length.   The power to be used depends on the nature of the lines to be measured: faint and fuzzy lines require a lower power than do sharp, definite lines.   Overmagnification, so that the line appears grainy and many times wider than the cross hair,

will result in less accurate measurements than will a power which gives a line image of reasonable width and sharpness.

The most troublesome systematic error of comparators is periodic error of the precision scale or of the screw and its bearings and scale drum. A test for the amplitude of the periodic error should be made on every new instrument, and, in the case of screws, it should be repeated occasionally so that if wear has altered the error the fact may be discovered. Since the periodicity, except for a possible slight progressive error of the screw, is one turn of the screw, the error will be revealed by successive measurements of the length of some object which differs considerably from one turn, the object being advanced after each measurement by one-tenth of the screw pitch until a whole turn has been covered. While any well-defined target will do, such as an ink spot or two scratches on a glass plate, two divisions 0.50 mm apart on a ruled scale or on a microscope micrometer disc make a convenient test object for a screw of 1-mm pitch. A little consideration will indicate that a test-object length of one-half the screw pitch will show the maximum effect. The observer should satisfy himself that he can repeat settings to about .001 mm and should average several settings on each position. The tests should be repeated on several turns at different parts of the screw, since the error is not necessarily uniform.

Table V shows a set of readings taken on a micrometer screw. The first two columns show the readings of the drum on the screw head at the two ends of the 0.50 length; the third column gives the apparent length of the object in terms of the screw; the fourth column is the error, or difference from the assumed length of 0.50 mm, in hundredths of a millimeter; the fifth column gives the same quantity in microns. Obviously, instead of deviation from the assumed length, deviation from the mean apparent length could equally well be used.

TABLE V
MEASUREMENTS OF A 0.50-MM SCALE AT DIFFERENT
DRUM POSITIONS

Initial Reading	Final Reading	Apparent Length	Error in $mm \times 10^{-2}$	Error in μ
00.12	49.95	49.83	−.17	−1.7
09.93	59.54	49.61	−.39	−3.9
20.01	69.76	49.75	−.25	−2.5
30.84	80.98	50.14	+.14	+1.4
40.07	90.32	50.25	+.25	+2.5
49.95	00.50	50.55	+.55	+5.5
59.95	10.50	50.55	+.55	+5.5
70.59	20.98	50.39	+.39	+3.9
79.96	30.08	50.12	+.12	+1.2
90.06	39.93	49.87	−.13	−1.3

Fig. 82 shows the error in microns from Table V plotted against the initial reading. Periodic error of the amount found in this screw will interfere with the accuracy of the results. The instrument should be

improved, if possible, to eliminate the error. Otherwise, mechanical compensation for the error will be necessary[22] or corrections must be applied to the measurements.[23] In a first-quality comparator, the periodic errors should have an amplitude of less than 1 micron and should thus be of the same order as the errors of setting.

Random errors may occur in screw-type comparators because of such faults as backlash, dirty or gummy lubrication between nut and screw, and change in the viscosity of the lubricant as a result of temperature changes. All of these faults manifest themselves in failure to repeat readings on sharp lines within the accuracy of the setting. Some provision is usually made for eliminating backlash, and it should not cause trouble if readings are always approached from the proper direction,
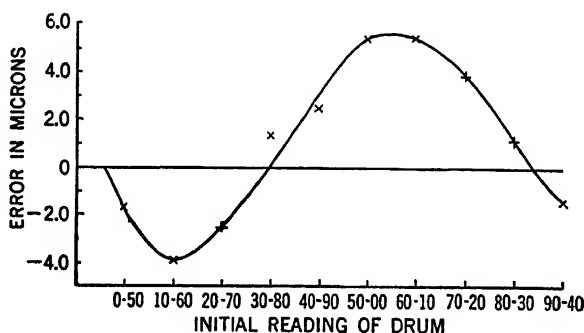
Fig. 82. Periodic Error of a Comparator Screw.

as indicated by the design of the instrument. Appearance of backlash in an instrument previously free from it is generally a sign of faulty lubrication. Improper lubrication may also result in a random or progressive variation of the thickness or viscosity of the oil film between screw and nut. Readings will then fail to agree if a line is remeasured after the nut has been run past it several turns. Lack of temperature equilibrium of the instrument will have a similar effect. It is best not to subject a comparator to wide temperature changes, since a long time is ordinarily required for equilibrium to be attained. A good test for random errors is to make a setting on a line near one limit of the travel of the nut, run the nut rapidly to the other limit of its travel, return it, and reset it on the line. Failure to repeat readings within the expected limits is an indication of random error. This test should be applied at the beginning of each set of readings and the source of any such error immediately located and removed.

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[22] G. R. Harrison, *Rev. Sci. Inst.*, **9**, 15, 1938, describes a method of automatically compensating screw errors.

[23] A. W. Gray, *Bur. of Stand. Bull.*, **10**, 375, 1914, discusses the testing of screws and correction of data; Rosenberg, *Zeits. f. Instrkde.*, **22**, 246, 1902.

88. Reduction of Prism Spectrograms

The determination of wave length by means of prism instruments is essentially a process of comparison with reference standards. This comparison is in some cases indirect and not immediately obvious, as in the case of the constant-deviation wave-length spectrometer (see page 85). Wave lengths observed in the eyepiece are read from a scale of helical or spiral form with an accuracy that depends on the wave-length region and on the particular instrument, but which is rarely better than 1A and, in the smaller instruments, is considerably less. Some fixed-position instruments, notably many single-prism quartz instruments, are fitted with wave-length or wave-number scales engraved on glass and arranged so that they can be printed on the photographic plate and developed with the spectra. The accuracy with which the scale can be read decreases toward longer wave lengths as the dispersion decreases. In the Hilger medium quartz instrument, for example, the accuracy is stated to be 1A at 2200A, 5A at 3000A, 20A at 4000A, and 100A at 7000A.

These built-in wave-length scales rest, of course, on calibration performed at the factory with the help of known standard wave lengths. If the instruments are not provided with such scales, and always if the best accuracy is needed, direct comparison must be made with known wave lengths recorded on the same photographic plate. The choice of these standards and of the manner of their introduction depends somewhat on the problems and equipment. For work of high precision, recourse must be had to the standards adopted by the International Astronomical Union or, in extreme cases, if these standards cannot be used, to other lines based on them. In the vacuum region, as noted above, no accepted standards exist, and care must be exercised in choosing a consistent set of reference lines.

Unless suitable reference lines appear in the spectrum, as, for example, gas-impurity lines in the vacuum region, they must be recorded on the spectrum plate from a separate light source. It is usual to record the reference, or comparison, spectra beside or overlapping the one to be measured, although they may be superimposed, with the lines of one spectrum much shorter than those of the other in order that they may be distinguished. With stigmatic spectrographs, which most prism instruments are, the location of the two spectra is effected by some form of Hartmann diaphragm before the slit, which alternately exposes parts of the slit to and protects them from the different radiations. With concave gratings and other astigmatic instruments, some form of occulting diaphragm is usually arranged before the plate so that adjacent strips may be exposed to the various spectra. If the spectra are adjacent, it is desirable that the two sets of lines meet or overlap. When a micro-

scope or comparator is used in measuring the lines, the junction line is placed in the middle of the field parallel to the traversing motion. The lines of each set are then measured at this line of junction and all difficulties due to line curvature are avoided. In stellar spectroscopy the lines of the star's spectrum are very short and it is not always possible to bring the stellar and reference spectra into juxtaposition. In that case, a correction for the relative displacement of the two spectra due to line curvature must be made with the help of the formula for the curvature, given previously (Sec. 31). It is to be noted that this correction varies with wave length, since the curvature is a function of the index of refraction and of the focal length of the lens.

Even in the case of contiguous spectra, difficulty sometimes arises in the use of a comparison spectrum because of a relative displacement of the unknown and reference spectra so that the unknown lines appear of too large or too small wave length.[24] If the collimator lens is not completely filled by each source, such a displacement may be the result of the illumination of different parts of the optics by the radiation from the reference and unknown light sources, since (see page 102), with imperfect optics, light passing through different parts of the optics may be brought to a focus at slightly different positions along the plate. The result may be a different line form for the two spectra, which will cause an error in measurement, or, in bad cases, two lines of identical wave length in two spectra may actually appear at slightly different positions on the plate. To avoid trouble from this cause, it is essential that the source of the reference lines be placed as exactly as possible in the position of the unknown light source, so that identical illumination of the optics by each is assured.

Relative displacements of the two spectra can arise also as a result of temperature or pressure shifts, which during long exposures may cause changes in the dispersion so that the lines are broadened and shifted. Other causes may be vibration or shocks which produce movement of the plate, of the slit, or, less probably, of the prism while the exposure is being made or while preparations are being made to change from one light source to the other. If a Hartmann diaphragm is to be moved on ways attached to the slit head, and if displacements of the slit are to be avoided, the slit must be rigidly mounted and the ways nearly frictionless. Displacements of the spectra will be recognized by the disagreement between the measurements of the same line on different plates, or by errors in the values of wave lengths of known lines in the unknown spectrum. The displacements are likely to be only a few hundredths of a millimeter; the resulting wave-length errors, while systematic,

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[24] The spectrum, wave lengths of which are to be determined, and its light source, will be referred to as the unknown.

vary in amount throughout the spectrum because of the changing dispersion in prism instruments.

After the lines of the reference spectrum and unknown spectrum have been measured, several procedures are available for obtaining the wave lengths of the unknown lines. The simplest, although not the most accurate or necessarily even the quickest, is graphical interpolation from a dispersion curve. This curve is constructed by plotting on cross-section paper the line measurements against the wave lengths for enough of the reference lines so that a smooth curve can be drawn through the points. A dispersion curve is convenient for rough identification—to an angstrom or so. If, however, the curve is to yield the utmost accuracy possible, it must be plotted on a very much larger scale. Spectral lines are ordinarily measured to about .001 mm; to show this graphically, the scale must be at least 1 mm on the paper per .01 mm read, or, in other words, 1 cm on the plate is represented by 1 meter on the curve. The scale must be large in the other direction to show tenths or hundredths of an angstrom. A very large sheet of graph paper is not needed if the curve is plotted in several slightly displaced and nearly parallel sections on a sheet perhaps one meter long.

From such a dispersion curve the wave lengths of the unknown lines can be read with considerable accuracy, but the labor of making such a curve is hardly justified unless a large number of wave lengths are to be determined. Even then, if they are on different plates, variations in dispersion from plate to plate because of changes in temperature and pressure, or the effect on plate and comparator dimensions of different temperatures at the time of measurement, will prevent the attainment of the highest precision possible.

Whenever the best attainable results are desired from prism spectrograms, resort must be had to mathematical interpolation between the reference lines. The calculation may be made either by linear interpolation between two nearby standards, or by the use of a dispersion formula over a wider range. Linear interpolation is based on the relationship

$$\lambda = \lambda_1 + \frac{\lambda_2 - \lambda_1}{d_2 - d_1}(d - d_1) \qquad (85)$$

where λ_1, λ_2 and d_1, d_2 are the wave lengths and microscope readings for the two reference lines, and λ and d the same values for the unknown. This calculation is readily made on a calculating machine (see page 237) or, for small ranges, since the second term represents a relatively small amount to be added to λ, it may often be read with sufficient accuracy from a slide rule. A sample calculation is given in Table VI. The linear formula, of course, assumes a constant dispersion over the range between the two standards, although this assumption is never exactly true and

<div align="center">

TABLE VI

CALCULATION OF WAVE LENGTHS BY LINEAR INTERPOLATION

$\lambda_1 = 2359.11$, $d_1 = 57.459$; $\lambda_2 = 2379.27$, $d_2 = 60.526$

</div>

$$\lambda = \lambda_1 + \frac{\lambda_2 - \lambda_1}{d_2 - d_1}(d - d_1) = 2359.11 + \frac{20.16}{3.067}(d - 57.459)$$

$$= 2359.11 + 6.5732(d - 57.459)$$

Intensity	d (mm)	$d - d_1$ (mm)	$c(d - d_1)^*$ (A)	λ (calc) (A)	λ (true) (A)	Error (A)
2	57.459				2359.11	
2	58.338	.879	5.78	2364.89	2364.83	.06
0	59.198	1.739	11.43	2370.54	2370.49	.05
3	60.388	2.929	19.25	2378.36	2378.33	.03
2	60.526	3.067	20.16	2379.27	2379.27	

$^*c = \dfrac{\lambda_2 - \lambda_1}{d_2 - d_1} = 6.5732.$

the error will increase with the range. For example, for the various quartz spectrographs manufactured by Adam Hilger, Ltd., Twyman[25] states that the error from the use of linear interpolation will be less than that introduced by the line measurements if the distance of the reference lines from the line measured does not exceed 20A at 6000A, 10A at 3000A, or 3A at 2100A.

89. The Hartmann Dispersion Formula

If many lines are to be determined, linear interpolation is rather laborious and requires the identification of many standard lines. Furthermore, the accuracy depends nearly equally on the accuracy of measurements of the two standard lines and on the accuracy of measurement of the unknown. The use of the Hartmann dispersion formula greatly reduces the number of lines to be identified in advance, and also minimizes the effect of an error in the measurement of a standard line. Reference has already been made (page 58) to this expression for dispersion. For wave-length calculation, it may be written:

$$\lambda = \lambda_0 + \frac{C}{d_0 - d} \qquad (86)$$

where λ_0, C, and d_0 are constants. This expression represents the dispersion curve of a prism spectrograph with a fair degree of approximation. The fit is somewhat better if $d_0 - d$ is replaced by $(d_0 - d)^{1.2}$, but the increased labor of computation is ordinarily not justified.

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[25] F. Twyman, *The Practise of Spectrum Analysis with Hilger Instruments*, 5th ed., p. 51. London: A. Hilger, Ltd., 1931.

It was pointed out by Hartmann that, while d_0 depends on the scale setting chosen, and C on the chosen range and region of the spectrograph, λ_0 is a constant of the spectrograph and should always have the same value for the same instrument. Actually, since the Hartmann formula does not exactly represent the dispersion of a prism, the value of λ_0 will vary somewhat with the choice of spectral range. Even for the same range, variations of a few per cent in λ_0 will be observed because of the effects of temperature, adjustment, and deviations in the measurement of the three standard lines.

For the determination of the three constants of the Hartmann formula, λ_0, C, and n, the comparator readings d of three lines of known wave length λ are needed. Several forms have been given for the solution of the three simultaneous equations resulting from the substitution, successively, of the three pairs of values in the formula.[26] A form found convenient at the University of Michigan for machine calculations is given below, with a numerical example.

$$\lambda_3 = 3307.25 \qquad d_3 = 141.950$$
$$\lambda_2 = 2813.29 \qquad d_2 = 109.646$$
$$\lambda_1 = 2327.39 \qquad d_1 = 52.431$$
$$\lambda_2 - \lambda_1 = 485.90 \quad d_2 - d_1 = 57.215$$
$$\lambda_3 - \lambda_1 = 979.86 \quad d_3 - d_1 = 89.519$$
$$d_3 - d_2 = 32.304$$

$$\frac{d_2 - d_1}{\lambda_2 - \lambda_1} = a = .1177506$$

$$\frac{d_3 - d_1}{\lambda_3 - \lambda_1} = b = .0913590$$

$$a - b = .0263916$$

$$\frac{d_3 - d_2}{a - b} = \frac{C}{d_0} = \frac{32.304}{.0263916} = 1224.03$$

$$\lambda_0 = \lambda_1 - \frac{C}{d_0} = 2327.39 - 1224.03 = 1103.36$$

$$d_0 = a(\lambda_2 - \lambda_0) = .1177505(2813.29 - 1103.36) = 201.345$$

$$C = \frac{C}{d_0} \cdot d_0 = 1224.03 \cdot 201.345 = 246452.3$$

If $d_1 \neq 0$, it is to be effectively reduced to zero by putting

$$\bar{d}_0 = d_0 + d_1 = 201.345 + 52.431 = 253.776$$

and

$$\lambda = \lambda_0 + \frac{C}{\bar{d}_0 - d} = 1103.36 + \frac{246{,}452.3}{253.776 - d}$$

[26] For example, W. F. Meggers in Glazebrook's *Dictionary of Applied Physics*, Vol. 4, p. 882. London: Macmillan & Co., 1923. E. C. C. Baly, *Spectroscopy*, Vol. 1, p. 141. London: Longmans, Green and Co., 1924.

If the scale readings of d decrease with increasing wave length on the plate, the last two expressions become:

$$\bar{d}_0 = d_0 - d_1$$

$$\lambda = \lambda_0 + \frac{C}{\bar{d}_0 + d}$$

It is desirable to check the solution by resubstitution, calculating λ_1, λ_2, and λ_3 from d_1, d_2, and d_3. Checking by calculation of one of these wave lengths is not sufficient, since, as may easily be shown, a check on λ_1 verifies the work only from the first subtraction of λ's and d's; λ_2 will check in spite of an error in $\lambda_3 - \lambda_1$ or $d_3 - d_1$, and λ_3 will check in spite of an error in $\lambda_2 - \lambda_1$ or $d_2 - d_1$. The λ_3 check in the example just given yields

$$\lambda_3 = 1103.36 + \frac{246452.3}{253.776 - 141.950} = 1103.36 + 2203.89 = 3307.25$$

In the divisions and multiplications necessary in the computation of the constants, it is well to carry one place more than the number to be determined in λ, that is, seven significant figures if six figures are wanted in the wave length.

If the range of wave length covered in the solution is as large as in the example above, the deviations of the calculated from the true wave lengths will be larger than the experimental error, and the calculated wave lengths should be corrected with the aid of a correction curve. This curve is constructed by plotting the corrections for a considerable number of known reference wave lengths against their wave lengths, and drawing the best smooth curve to fit the points. Such a curve is shown in Figure 83, for the plate for which the constants are calculated above.

The scatter of the points about the curve is an indication of the accuracy of the wave-length determination from the measurements, since the scatter should be wholly due to the uncertainty of measurement and may be expected to be about the same for the unknown as for the reference lines. The scatter will, in general, be greater toward the long-wave length end of the curve, where the decreasing dispersion leads to larger wave-length deviations for the same accuracy of measurement. The two halves of the curve will be nearly equal in amplitude if the central standard line divides the wave-length range between the two outer standards into two approximately equal parts. A failure of the error to fall to zero at the three standard wave lengths, that is, to pass through these three points on the wave-length axis, indicates an error in the identification or measurement of one or more of these lines. Such failure does not necessarily invalidate the wave-length calculations. The curve is still usable, although the corrections to be applied may be larger than in the ideal case. It is to be noted that the correction curve, since it is

the best fit for a considerable number of points, may be better than the individual measurements on any or all of the standards and may minimize the effects of errors in these measurements.   The final uncertainty in the calculated values of an unknown wave length should be fixed almost wholly by the measurement on the line itself.   The magnitude of the correction increases very rapidly for lines falling outside the range of
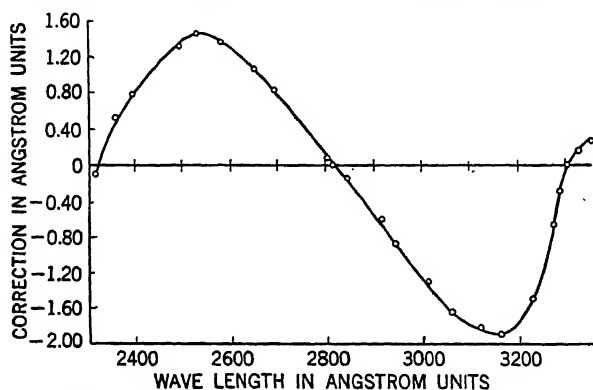
Fig. 83.   Corrections to Hartmann Dispersion Formula.

the two outer standard lines.   It is best to use a Hartmann formula for a range which is little, if any, greater than that of the standards.

The calculation of wave lengths from the formula involves three steps: one subtraction or addition, $d_0 \pm d$; one division, $C/(d_0 \pm d)$; and, finally, the addition of the quotient to λ_0.   Each of these steps can be completely carried out on a calculating machine, but it has been found that time is saved if, after the quotient is obtained on the dials, it is added mentally to λ_0, the value of which has been written on a slip of

TABLE VII

CALCULATION OF WAVE LENGTHS BY THE HARTMANN FORMULA

$$\lambda = 1103.36 + \frac{246,452.3}{253.776 - d}$$

Origin	Intensity	d (mm)	$d_0 - d$ (mm)	$\dfrac{C}{d_0 - d}$ (A)	λ (calc) (A)	Correction (A)	λ (corr) (A)
Fe......	2	53.307	200.468	1229.38	2332.74	.07	2332.81
In......	5	56.153	197.622	1247.08	2350.44	.28	2350.72
Hg......	3	60.388	193.387	1274.39	2377.75	.58	2378.33
Fe......	2	60.526	193.249	1275.30	2378.66	.61	2379.27
He......	0	61.447	192.332	1281.38	2384.74	.72	2385.46
Fe......	2	63.480	190.295	1295.10	2398.46	.78	2399.24
In......	10	71.975	181.800	1355.62	2458.98	1.15	2460.13
Fe......	3	73.139	180.636	1364.35	2467.71	1.17	2468.88

The iron lines are identified from wave-length tables, and the corrections, λ (table) $- \lambda$ (calculated), used to draw the correction curve, Fig. 83.   The indium, helium, and mercury lines are from the unknown spectrum.   The mercury line is recognized as an impurity.

paper and placed on the machine carriage above the dials. The work is best arranged on a sheet with parallel columns for the comparator measurements, each of the steps of the calculation, the corrections to the calculated wave lengths, the final wave lengths, and, a last column, notes, identifications, and so forth. For convenience in calculation, each step is carried through on all measurements before the next step is begun. A sample sheet showing the calculation of a few wave lengths is given in Table VII. The data are taken from the same plate for which the Hartmann solution was previously given—a plate on which an iron comparison spectrum was used for the determination of wave lengths in a hollow cathode discharge spectrum of indium operating in a helium atmosphere.

The calculation of wave lengths by the Hartmann formula is rather tedious, involving as it does three distinct steps. It was pointed out by King[27] and later by Fowler and Eagle[28] that by a geometric projection the relation between displacement on the plate and wave length could be made linear for a prism spectrograph, and that the reduction of plates could thereby be greatly simplified. The principle is illustrated in Figure 84, which shows one of the numerous possible projections. The wave lengths of

Fig. 84. Geometric Projection to Render Prismatic Dispersion Linear.

the spectral lines λ_1, λ_2, and λ_3 and of λ_0 of the corresponding Hartmann equation are laid off linearly on one line, and the corresponding scale readings, d_1, d_2, and d_3 and the constant d_0 are laid off on another line intersecting the first line at an arbitrary angle α. Lines are drawn through d_0 parallel to the λ-line, and through λ_0 parallel to the d-line. The intersection of these lines determines a point P such that any point d_1 is projected into the corresponding λ by a straight line $d_1P\lambda_1$. This follows since the triangles d_0d_1P and $\lambda_0P\lambda_1$ are similar. Hence, expressing the distances on the scales as differences of scale readings, $(\lambda_1 - \lambda_0)/d_0P = \lambda_0P/(d_0 - d_1)$, or $(\lambda_1 - \lambda_0)(d_0 - d_1) = K$, which is the Hartmann formula.

Various methods have been proposed for carrying out this geometric projection. King photographed the spectrum plate at such an angle and camera distance that the new spectrogran obtained had a linear dispersion. Grassmann[29] carried out the projection graphically, using a ruler pivoted at the projection point to find the wave length on the λ-scale corresponding to a line on the plate (d-scale). The accuracy is

[27] E. S. King, *Science*, **8**, 454, 1898.
[28] A. Fowler and A. Eagle, *Astrophys J.*, **28**, 284, 1908.
[29] P. Grassmann, *Phys. Zeits.*, **32**, 149, 1931.

limited, of course, by the accuracy with which the plotted wave-length scale can be read.

An application of the projection principle which does not result in loss in precision of the wave-length determination is that of Hoxton and. Mann.[30]   They have constructed a comparator in which the usual direct coupling of the screw to the plate carriage is replaced by a simple mechanical. linkage.   This linkage performs the projection in such a way that, as the microscope cross hair is set on the spectral lines, the comparator-scale readings of the screw settings bear a simple linear relationship to the wave-length interval traversed.   For example, the adjustment may be such that one millimeter on the screw is equivalent to ten angstroms.   If the plate is adjusted so that the scale reading for λ_1 is zero, wave lengths are then computed by adding to λ_0 ten times the comparator reading on any line.   The linkage can be adjusted to operate for almost any range of any spectrograph.   Even with grating spectrograms, where the wave length-displacement relationship is already practically linear, the comparator has the advantage of providing a simpler conversion factor.   The results delivered by the comparator are subject to the same shortcomings as those obtained by calculation from conventional comparator readings, and they must be corrected similarly by a correction curve constructed from the deviations for a series of known reference lines.

90. Wave-Number Determination

. The procedures heretofore described have all been for the calculation of wave length. In some respects the calculation of wave number—the number of wave lengths in one centimeter in vacuum—is somewhat more readily carried out.   If a dispersion curve is used for the reduction of the prism spectrum, it is found that the wave-number curve is considerably straighter than the wave-length curve, and is therefore somewhat easier to use, even if on a smaller scale.

Since the wave-number curve is straighter, linear interpolation in wave numbers can be carried out with the same accuracy over longer intervals than can interpolation in wave lengths.   This fact has led Russell and Shenstone to investigate the possibility of a quadratic formula for wave-number calculation.[31]   It was found that for some spectrographs, especially single-prism, one-material instruments, a simple form of equation is satisfactory,

$$\nu = \nu_0 + ax + A - b(x - x_m)^2$$

in which ν_0 is the wave number of the standard of longest wave length; a is the wave number per centimeter for the full range used; A is the

[30] L. G. Hoxton and D. W. Mann, *J. Opt. Soc. Am.*, **27**, 150, 1937.
[31] H. N. Russell and A. G. Shenstone, *J. Opt. Soc. Am.*, **16**, 298, 1928.

maximum value of the curve of $(\nu - \nu_0 - ax)$ plotted against x; x_m is some point near the center of the range; b is A divided by x_m^2. It will be seen that this expression may be thought of as a linear interpolation formula with a quadratic correction term. The linear interpolation is easily made on a calculating machine, and the quadratic correction term can be computed with sufficient accuracy on a twenty-inch slide rule. Like the Hartmann formula, this expression will fit exactly only at each end and in the middle of the range. A correction, or residual curve, which must be plotted from results on known lines, will be needed to correct the computed wave numbers. The process is considerably more rapid than the corresponding calculation and correction of wave lengths by the Hartmann formula.

The projection methods described earlier for converting prism spectra to a linear wave-length scale can also be used for obtaining a linear scale of wave numbers. The Hoxton and Mann comparator is also adaptable to wave-number determination. It can be adjusted so that the readings bear a linear relation to the wave-number interval traversed, say 50 wave numbers per mm of scale, so that wave numbers are obtained by a simple addition process similar to that for wave lengths.

For work in the analysis of spectra where wave numbers rather than wave lengths are used, the direct calculation of wave numbers saves the additional step of converting wave lengths to wave numbers that would otherwise be required. For most other work, wave numbers would be as useful as wave lengths if spectroscopists were accustomed to thinking in these terms. At present, practically all charts and tables of spectral lines give wave lengths only or primarily. Thus, the use of standard wave lengths, the checking of results for impurities, and the comparison with the work of other investigators are extremely difficult when spectrograms are reduced directly in terms of wave numbers.

91. Reduction of Grating Spectrograms

Although in the case of grating spectrograms the absolute determination of wave lengths is possible by the substitution of the value of the grating space and angles in the grating equation, $n\lambda = d(\sin \alpha + \sin \beta)$, this procedure does not produce highly accurate results. The first wave-length standards were arrived at in this way (Sec. 7), and the first determinations in the extreme ultraviolet[32] were of necessity so made. In the infrared, beyond the photographic limit, calculations are based on the wave length of one known line and the known constants of the apparatus. At present, however, in practically all photographic spectroscopy the grating, like the prism spectrograph, is used for the

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[32] R. A. Millikan and R. A. Sawyer, *Phys. Rev.*, **12**, 167, 1918.

determination of wave lengths by comparison with standard reference lines.

Unless the reference-spectrum lines are present· in the unknown spectrum, as is sometimes the case, provision must be made for recording separately and differentiating the two spectra. In plane-grating spectrographs and in the stigmatic mounting of the concave grating, a Hartmann diaphragm can be used to place the unknown and comparison spectra in juxtaposition. All concave grating mountings based on the Rowland circle exhibit astigmatism to a greater or less degree (see ·Sec. 50), and some other means must be used to separate the two spectra sharply. Some form of occulting diaphragm placed just before the plate is the commonest method. Various arrangements of this kind will be found in the literature in descriptions of grating installations.

If the astigmatism is not too great, the overlapping of two spectra, separated by a Hartmann diaphragm at the slit, may be small enough to permit the use of this method of impressing comparison spectra. In fact, a slight overlapping may help in making possible the measurement of both spectra along the same common line.

Another method for differentiating the reference and unknown spectra, or for producing two sharply defined adjacent spectra, was first pointed out by Sirks (Sec. 50). In the Rowland mounting a horizontal line, if placed before the slit on the tangent to the circle at the grating normal, will be sharply imaged on the circle at the normal. A diaphragm or comparison prism may be placed at this point. Analogous constructions[33] may be made for cases where the spectra are to be photographed at points other than near the grating normal.

With concave grating mountings based on the Rowland circle it is sometimes convenient to make use of overlapping orders in introducing reference lines. As is seen from the grating equation (page 123), all wave lengths for which the product of order times wave length has a given value are brought to a focus at the same point on the circle. It is then possible to compare, by the coincidence of overlapping orders, unknown spectra in one order with higher or lower orders of reference spectral lines which fall in the same region on the circle. Rowland used this method in establishing his tables of wave-length standards, and its dangers became apparent when Rowland's wave lengths were found to have systematic errors.[34] Michelson[35] showed that imperfect gratings could give a different line form in different orders, with a resultant relative displacement of the lines of different orders. Kayser[36] found

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[33] C. Runge and R. Mannkopf, *Zeits. f. Physik*, **45**, 13, 1927; G. H. Dieke, *Proc. Sixth Summer Conference on Spectroscopy*, p. 71. New York: John Wiley & Sons, 1939.
[34] H. Kayser, *Astrophys. J.*, **13**, 331, 1901.
[35] A. A. Michelson, *ibid.*, **18**, 278, 1903.
[36] H. Kayser, *ibid.*, **19**, 157, 1904, and **20**, 327, 1904.

that such effects occurred in his gratings. While not all gratings are subject to this defect, great caution must be exercised in the use of the coincidence method. It is necessary to satisfy oneself that appreciable errors are not introduced by the grating used, and since the error, if present, is largely influenced by the adjustment, the grating must be tested after it is focused.

The calculation of wave lengths from grating spectrograms, once the reference lines have been identified, is simpler than for prism spectrograms because of the greater constancy of the dispersion. The dispersion (see p. 132), $n/d \cos \beta$, is a minimum for $\beta = 0$, and varies relatively slowly with $1/\cos \beta$ as β increases. With a concave grating, for a distance p from the grating normal the error arising from assuming normal dispersion is $dp^3/24nr^3$,[37] where d is the grating space, n the order, and r the radius of curvature of the grating. Accordingly, for a grating of 15,000 lines per inch, or 6000 per cm, and a radius of curvature of 630 cm, putting the error at $.001A$ and solving for p, in the first order,

$$p^3 = \frac{1 \times 10^{-11} \times 24 \times (630)^3}{.000167}; p = 7.1 \text{ cm}$$

Or, for a plate extending 7.1 cm, or about 185A on either side of the normal in the first order, the spectrum is normal to within the accuracy of measurement. Similar calculations can be made for other mountings and conditions.

As soon as a few reference lines on a grating plate have been identified, linear interpolation with the aid of a steel millimeter scale and a slide rule will quickly give a rough calculation of other lines for identification purposes. For accurate wave lengths, of course, the lines must be carefully measured with a comparator. Linear interpolation over appropriate ranges by Formula (85),

$$\lambda = \lambda_1 + \frac{\lambda_2 - \lambda_1}{d_2 - d_1} (d - d_1)$$

is generally preferred for final calculation because of its simplicity.

An example of such calculation has been given in the section on the reduction of prism spectrograms (page 228). The calculations may be made very simply with a machine of the Fridén, Marchant, or Monroe type. After the grating constant $(\lambda_2 - \lambda_1)/(d - d_1)$ is determined, the machine is set up as follows: The reading on the first standard line d_1 is set on the upper, or operation-counting, dials, with the decimal point set so that operations will be counted in the unit place. λ_1 is set on the lower, or summation, dials, and 5 is added in the place beyond the last significant figure to take care of rounding off. The grating constant is

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[37] H. Kayser, *Spectroscopie*, Vol. I, p. 466.

set on the keyboard so that its decimal point is in line with that of λ_1 on the lower dials. If the formula is, for example,

$$\lambda = 1084.99 + \frac{1331.76 - 1084.99}{46.519 - 32.350}(d - 32.350)$$
$$= 1084.99 + 17.4162(d - 32.350)$$

the upper dials are set at 32.350, the lower dials at 1084.995, the keyboard at 17.4162, and the machine is set for multiplication. If the plus key is struck once, 17.4162 is added to the lower dial reading, which becomes 1102.4112, or rounded to six figures, 1102.41, and the upper dials read 33.350, the correct d for this wave length. If, now, the carriage and the plus and minus keys are manipulated to bring any value of d on the upper dials, the proper λ (plus .005) will be read on the lower dials. Then, without resetting the machine, all wave lengths in the range can be rapidly run off. If the comparator readings are made so that d decreases as λ increases, the formula becomes

$$\lambda = \lambda_1 + \frac{\lambda_2 - \lambda_1}{d_1 - d_2}(d_1 - d) \qquad (85A)$$

The procedure is the same except that the machine is set for division instead of multiplication. Striking the plus key then increases the lower dial reading, or λ, while decreasing the upper dial reading, or d.

Deviations from the calculated values should be tabulated, and, if larger than the error of measurement, should be plotted to form a correction curve. For small values of the diffraction angle β, the curve should be smooth and regular, the corrections being due almost wholly to the departures from linearity in the dispersion, ·if and when this departure is appreciable. For values of β near 90°, as in glancing-angle vacuum spectrographs, irregularities in the glass or in the form of the plate holder may lead to nonsystematic errors which give a quite irregular shape to the correction curves.[38]

It may not always be possible to find reference lines close enough together so that a satisfactory correction curve can be drawn for glancing-angle spectrographs or even, sometimes, for other grating mounts with smaller values of β. Usually the simplest procedure, then, is to use a second-order equation of the form

$$\lambda = \lambda_1 + a(d_1 - d) + b(d_1 - d)^2 \qquad (87)$$

The constants can be determined by substitution of the λ's and the d's for three known lines. The calculation of the first two terms can be carried out on a machine, as described above. The quadratic terms will generally be so small that they can be read from a slide rule with sufficient

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[38] B. Edlen, *Nova Acta Reg. Soc. Sci. Upsal.*, **9**, 1, 1934.

accuracy.   Jeppeson[39] has described a least square method of getting the best second-degree equation.   Ericson and Edlen have used an adaptation of the trigonometric grating equation.[40]

The Hoxton and Mann comparator, described earlier (page 234), for use in the reduction of prismatic spectra, can be used also to eliminate the use of reduction formulae with grating spectra.   It can be set either for a linear or a second-order formula, and will deliver readings which need only to be multiplied by a simple factor, such as 10 or 50 A/mm, and added to the reference wave length.   The deviations of the resulting wave lengths from those of the reference lines should be tabulated and a correction curve drawn if necessary.   Wave numbers can also be obtained directly if desired.

The Harrison automatic comparator and microphotometer, referred to elsewhere (page 221), which measures, computes, and records up to 2000 wave lengths per minute, is the most effective reduction process yet perfected for grating spectrograms.   A steel correction template can be cut and used in the reducing mechanism for each plate setting of the grating, and thus the need for individually plotted correction curves can be eliminated.

92. Identification of Lines and Bands

In many applications of spectroscopy, the atom or molecule responsible for the various lines or bands in a spectrogram must be determined. Thus, the question may arise, What atoms or molecules are present in the light source, and what is their stage of excitation or ionization, or their abundance?   Or, again, it may be essential to know whether the lines emitted represent previously unknown radiations from the source materials, such as higher-series members, or new bands or radiations from new energy levels; or whether they represent impurities or contaminations in the electrode or discharge materials.

A somewhat more specific problem is that of deciding whether or not an atom or molecule is present in the electrode or discharge material. This problem requires some knowledge of the excitation possibilities of the source and information on the sensitivity of the spectroscopic apparatus used and on the excitation probabilities of the spectral lines or bands involved.

The problems outlined above arise in the practice of qualitative and quantitative spectrochemical analysis, in the analysis of series spectra, in spectroscopic study of discharge through gases, in astrophysical spectroscopy, and, in fact, in any application of spectroscopy where the character or nature of the radiations comes into question.   In all such cases, the

[39] C. R. Jeppeson, *Phys. Rev.*, **44**, 170, 1933.
[40] B. Edlen and A. Ericson, *Zeits. f. Phys.*, **59**, 656, 1930.

spectroscopist must be prepared to determine whether or not a particular kind of atom or molecule exists in the light source and to what source a particular line or band is to be attributed.

The identification of an individual spectral line or band, and the allied problem of the determination of the presence or absence of an atom or molecule in the radiation under consideration, require a study of the possibility of "disturbing" lines or bands, that is, radiations of other elements or molecules very close to that in question. Since, as already noted (page 217), the M.I.T. list of the stronger spectral lines of the elements in the range 10,000A–2000A contains 100,000 lines, or an average of about 12 lines per angstrom unit, clearly only an instrument of the largest dispersion could determine the wave length of a single line with sufficient accuracy to fix its origin unequivocally, even if sufficiently accurate and all-inclusive spectral tables of all the elements were available. Actually, it is necessary, in many cases, to consider all the possible sources for a particular line and to decide which of the various possibilities are to be expected in a given case.

In most cases, the major constituent or constituents of the discharge are known or are readily determined by inspection of the strongest lines or bands. Most of the other lines belonging to these constituents can then be identified by the use of the tabulations of spectra and a consideration of their known relative intensities in the same or similar light sources. It may also be desirable to photograph, with the same light source and equipment, the spectra of pure samples of the major constituents and thus facilitate a rapid identification of all their lines.

After this procedure the lines left unidentified are generally rather weak. They are probably either hitherto unobserved lines of the major constituents or lines of unidentified minor constituents. If the latter, they must be among the stronger lines of these substances. To determine what these substances are, in the case of atomic spectra, valuable sources of information are the lists and charts of the most sensitive lines of the elements, that is, the lines which appear in the spectrum when only traces of the element are present in the source. Such charts have been discussed in the section on "Spectroscopic Charts and Tables" (page 214). The Bardet chart for prismatic spectra and that of Crook for grating spectra are especially useful for orientation purposes in the regions they cover. Along with a wave-length scale, they show the sensitive lines of many elements in juxtaposition with an iron spectrum.

In the case of an emission line, comparison of the charts or tables of the principal lines of the elements will show whether or not there is a close coincidence with any of the sensitive lines of any other element. Often a knowledge of the source under investigation will aid in deciding whether or not the presence of a particular element is probable. In any case, further verification must be sought in the form of additional

lines of the element in question.   Spectra of pure samples are of some use, but more helpful are lists or charts of the lines of the elements showing their order of disappearance with diminishing amount.   Such a chart is that of Lowe (page 214), showing spectra from a small quartz instrument, of 1, .1, .01, and .001 per cent of each of 44 elements in solution on graphite electrodes.   Tables with similar information are those of Twyman and Smith (page 216).   If all, or nearly all, of the lines which should accompany a tentatively identified line of an element are found with proper relative intensities, the line may be assumed to be properly identified and the presence of the element established.   Similar corroborative evidence may often be gained from a consideration of the classification of the lines of a particular element.   If all the other lines of a multiplet or line group appear, or if the earlier members of a series are found accompanying tentatively identified lines which are higher members of the same series, again its identification may be accepted with confidence.

Sometimes, however, the major constituent has a great number of lines which obscure many of the corroborative lines sought, or it may be that the suspected element is present in so small a trace that only its most sensitive or persistent lines appear.   Recourse must then be had to a process of elimination of other elements which might have radiated the lines in question.   Consultation of the tables of principal lines, such as the M.I.T. or Kaiser-Ritschl tables, with due consideration of the dispersion of the spectrogram and of the type of source used, will reveal which elements have lines close enough to interfere.   These elements must then be considered in turn, and their presence, or that of the one originally suspected, established.   The consideration of interfering lines can be simplified by the use of the tables of Gerlach and Riedl,[41] which give, for each of the detection lines of 57 elements, the interference lines which must be considered, as well as decisive criteria for their identification.   These tables were made for use with a small quartz spectrograph, and so include interfering lines which would not be close enough to cause trouble if an instrument of larger dispersion were used.

With such tables as these, or any list of lines used to check interfering lines, it should always be remembered that the character of the light source must be taken into consideration.   The number and intensities of the lines of an element which appear in a spectrum depend on the light source used and to a considerable extent upon the other elements present in appreciable quantities.   Accordingly, some judgment is necessary in interpreting the indications, since there are wide variations in the relative spectral sensitivities of different elements and different light sources.

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[41] W. Gerlach and E. Riedl, *Chemical Emission Spectrum Analysis.*   London: C. Zeiss, 1938.

By the methods described it is generally possible to account for all but the weakest emission lines in any spectrum. These weak lines may be faint lines of some element in the source which appear by reason of particular excitation conditions that did not exist in the light sources used in compiling the reference tables. Thus, in gaseous discharges, there may be a resonance between the energy levels of these lines and one or more of the prominent energy states of the major constituent of the discharges. Again, the lines may be lines whose appearance is ordinarily "forbidden" by the selection rules for transitions between the atomic energy levels, but which can appear in the source used because of the electric or magnetic fields in the discharge. In arcs, weak lines may be heads or members of bands too weak to appear as bands; in sparks, lines from the surrounding gas may be weakly excited and difficult to identify.

Band lines are sometimes more difficult to account for than atomic lines, because the bands of all the many molecules in their different excited and ionized states are not so completely known and resolved as the atomic lines. Also, the number of bands and the number of terms in any particular band of a molecule excited by a discharge depend to a marked extent on the excitation, temperature, and other conditions of the discharge.[42] A further difficulty arises from the fact that many bands, by virtue of their structure, do not have sharp heads. The wave length of the apparent head depends, then, on the strength of the band and on the excitation conditions. Identification of such bands depends to a large extent on a knowledge of the probable constituents of the source and of the source conditions, and on the corroborating evidence of other bands of the same system. It is, in fact, always safest to make identifications, when possible, of band systems rather than of single bands.

The M.I.T. tables (page 217) give, among the atomic lines, the wave lengths of 1381 of the more common band heads that are most likely to be found in arc spectra. The tables of Pearse and Gaydon are also very useful in identifying bands. They give not only the principal bands of many molecules arranged by wave length, but also descriptions of the band systems of a large number of the more common molecules.

The procedure in the identification of bands is much the same as in the identification of line spectra. Tentative identification of parent molecules can be followed by a search for the band groups which should accompany the tentatively identified bands. In many cases much help can be obtained from a knowledge of the type of discharge and of the molecules likely to be present. Thus, the various CO and CO^+ bands and the OH bands are commonly found in gaseous discharges, and the N, O, and CN bands are found in arcs.

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[42] K. Herzberg, *Zeits. f. Physik*, **49**, 761, 1928.

A considerable amount of judgment and experience is an invaluable aid in the identification of unknown lines and bands.   It should be possible with care and judgment to avoid all but infrequent errors in identification.   Above all, it must be remembered that a single line is rarely a good criterion of the presence of an atom or molecule, and that it is best to be conservative in identification.

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Whitehead, T. N., *The Design and Use of Instruments and Accurate Mechanism*, Ch. IX.   New York: The Macmillan Company, 1934.   A discussion of design problems and desirable characteristics of comparators.

CHAPTER 10

The Determination of Spectral Intensity

For most spectroscopic work, information as to the intensities of the various parts or lines of the spectrum is desirable. How accurate this information needs to be depends on the purpose for which it is to be used. In some cases, as in series classification of spectral lines, a rough visual estimate suffices. For quantitative spectrochemical analysis, the demand is for accurate determinations of the comparative intensities of lines usually differing relatively little in wave length as they emerge from the spectroscope or spectrograph. In a third type of work, as in the rating of light sources or of therapeutic lamps, the actual spectro-radiometric distribution of the energy at the light source must be known; that is, correction for losses in the optical system must be made so that the incident energy distribution can be deduced from measurements of the emergent energy.

Many methods—direct and indirect, subjective and objective—have been proposed for determining relative or absolute spectral intensities.[1] Only the more important procedures and instruments will be discussed here.

93. Visual Photometric Methods

In the visible region, visual determination of intensity is the most direct procedure, although not the most accurate or even always the most rapid. It may be made with any type of instrument fitted for ocular observations, and may or may not involve the use of a visual photometer. Eye estimates alone are satisfactory where only rough accuracy is desired. It must be remembered, however, that such estimates are only approximate and, also, that if any considerable wave-length range is involved, their accuracy is further affected by the variation in the sensitivity of the eye with the wave length. The eye is sensitive, under normal conditions, to wave lengths ranging roughly from 4000A to 7600A (but see page 12), and within this range the relative sensitivity varies by a factor of 1000 or more (Fig. 85), being at a maximum at about 5500A and falling to zero at either end. Visual estimates of the intensity of spectral lines are comparable, then, only over a very limited wave-length range.

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[1] See Bibliography at end of chapter.

Quantitative intensity measurements can be made visually by combining some kind of photometer with the spectroscope.   Arrangement is usually made for viewing a divided field, in the two parts of which are seen simultaneously the unknown and a comparison spectrum.   The brightness of one or both parts of the field can be varied in a measurable manner until both are equally bright.   Such a brightness match can be
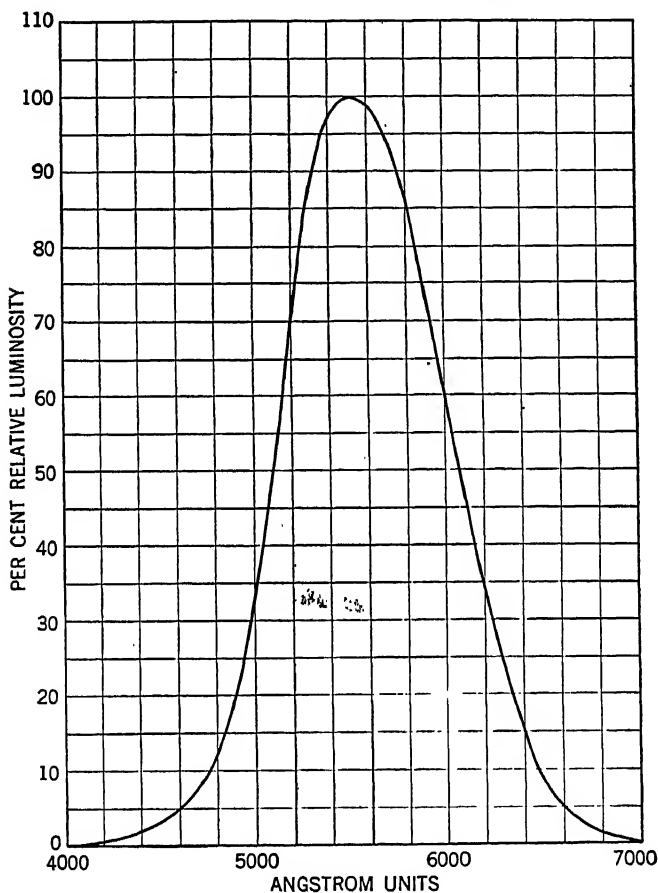
Fig. 85.   Spectral Sensitivity of the Average Human Eye.

made with much better precision than can an estimate or determination of absolute brightness.

If the instrument is intended for the measurement of the spectral transmittance or reflectance of a sample or for the measurement of the spectral energy distribution of a light source, the two fields are illuminated by beams which have been differentiated before entering the slit. For such reflectance or transmittance measurement, a beam from a suitable source is divided into two parts, the path of one including the

sample under test, the path of the other including a comparison, or standard, sample. For spectroradiometric study of a light source, one of the two beams comes from the source under examination, the other from a standard, or reference, source of known energy distribution.

Various means are used for altering the beam intensities[2] to obtain a match. A popular system is the Martens photometer, in which the two beams are polarized at right angles to one another by a Wollaston prism. The two beams, polarized on mutually perpendicular planes, then pass through an analyzing Nicol prism. By rotation of this prism, the two
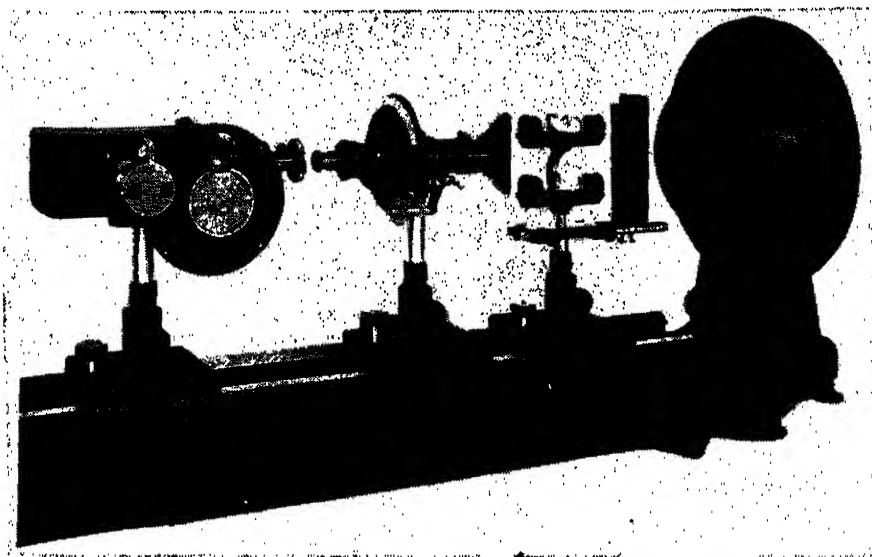
Courtesy of the Gaertner Scientific Corporation.

Fig. 86.   Polarizing Spectrophotometer Arranged for Transmission of Liquids.

beam intensities may be varied and matched and the position of the plane of transmission at the match point observed. The ratio of the intensities of the two beams is $\tan^2 \alpha$, where α is the angle between this plane and the plane of polarization of the weaker beam. The whole photometer may be placed before the entrance slit of the dispersing spectrometer; or the Wollaston prism may be placed before the slit, and the analyzing Nicol prism placed in the spectrometer eyepiece; or the photometer may be built into the collimator of the spectrometer. The first arrangement has the advantage that the spectroscope and photometer may be separate instruments and so be available for other uses.

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[2] For a fuller description of spectrophotometers, see the article by K. S. Gibson in *The Measurement of Radiant Energy*, W. S. Forsythe, ed., p. 326. New York: McGraw-Hill, 1937.

Fig. 86 shows a spectrophotometer by the Gaertner Scientific Corporation, comprising the constant deviation spectrometer described on page 84 and a Martens polarizing photometer.

Spectrophotometers similar to that just described are useful for comparing the spectra of two light beams line by line or, in the case of continuous spectra, point by point. The accuracy depends on the skill of the operator in matching the brightness of the two fields and, because of the spectral response characteristics of the eye, on the brightness and the color to be matched. Under the most favorable conditions, mean errors of 1 per cent or less are attained, although errors up to perhaps 5 per cent are more common.

For quantitative spectrochemical analysis by the internal-standard method, two lines of slightly different wave length in the same spectrum are compared, rather than lines of the same wave length in two different spectra. To make such a comparison visually, it is necessary to split the beam entering the spectroscope so as to obtain two juxtaposed spectra, one above the other, which can be displaced laterally with respect to one another and varied in intensity in a measurable manner. The chosen line in the upper spectrum can then be brought directly over the second line, in the lower spectrum, and the stronger line weakened in intensity until an intensity match is obtained.

Visual photometers which accomplish such a displacement and matching of two lines in a spectrum have been described by F. Twyman[3] and by Scheibe and Limmer.[4] The Twyman design, which uses a neutral wedge of variable density to match the intensity of the two lines, was formerly manufactured by the firm of Adam Hilger, Ltd. At present, neither of these devices is on the market.

94. Objective Photometric Methods

In regions where the eye is not sensitive, and in the visible region if many measurements are to be made or if better than visual accuracy is desired, various devices for the objective measurement of radiation find application. These detectors include thermopiles, photocells, and Geiger counters. They may be substituted for the eyepiece in any visual spectroscope or may be suitably mounted on a screw carriage moved along the focal plane of a spectrograph. If, like the thermocouple-galvanometer combination, the detector is both linear and nonselective in response, the observations give directly the relative intensities of any lines, regardless of wave length. Other detectors, however, like the photoelectric cell, are selective in their spectral response and may not be

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[3] F. Twyman, *Trans. Opt. Soc.*, **33**, 176, 1932.
[4] G. Scheibe and G. Limmer, *Metallwirtschaft*, **11**, 107, 1932.

strictly linear in response to intensity. Their readings must be suitably corrected to give intensities in comparable units for all wave lengths.

In the infrared region, one of these physical detectors of radiation must be used; in the near infrared, visible, and ultraviolet regions, photographic recording is often preferred because of its greater sensitivity and convenience. Intensities can be determined from the spectrogram, but since the photographic emulsion has both a selective and a nonlinear response to radiation, calibration is required to obtain quantitative intensity determinations. The methods for determining and interpreting these responses will be treated after the discussion of methods for measuring photographic density.

For such purposes as the identification of impurities or the classification of series, only a rough qualitative record of the relative intensities of neighboring lines is needed. Such information is obtained most simply by visual estimates of photographic line intensity, such as are commonly recorded when spectrograms are measured with a comparator. Most observers use a scale ranging from 1 or 0 for the weakest, or barely visible, lines to 10 for the strongest lines, although some have used scales running to 1000 or more. The actual range of line intensities in any extended spectrum is more than 1000 to 1, perhaps even 1,000,000 to 1; for such extreme ranges, the ordinary photographic plate exhibits a broadening of the strongest lines as well as an increase in their density. The response of the plate to intensity changes is approximately logarithmic (see page 185) and a scale of estimated intensities from 1 to 10 is probably roughly a logarithmic scale, but to some base much less than 10. Estimated intensities have little significance except for short ranges of wave length, both because of the dependence of the sensitivity of the photographic plate on the wave length, and the variation of contrast with different plates, and because of the inability of the eye to carry an absolute scale of intensities over a considerable time. Kayser[5] met this last difficulty by arranging to project into one half of the field of view of his comparator microscope ten lines which had been recorded on a photographic plate by exposure to the light of a narrow slit for 1, 2, 4, 8 . . . seconds. This range of intensities, logarithmic with base 2, gave him a fixed intensity scale, which, however, he found too steep at the low intensities and too flat at the higher.

The quantitative determination of intensities from spectrograms calls for a means of measuring the density of the photographic image. Some form of photometer is usually used to measure the amount of light transmitted by the silver deposit, and if the area to be measured is that of a small slit or circular aperture, the instrument is called a *microphotometer* or *microdensitometer*. In these instruments the plate is traversed by

[5] Kayser, *Handbuch der Spectroscopie*, Vol. I, p. 645. Leipzig: S. Hirzel, 1900.

a beam of light from a constant light source, and means are provided for comparing the brightness of the beam which has passed through the selected part of the emulsion with that of the same or of another part of the beam which has passed through a clear part of the plate.

From the readings, photographic density is computed by $D = \log I_0/I$, where I_0 is the light intensity of the measuring beam incident on the plate, and I that transmitted by the selected area on the plate. The measurements required are d, the clear-plate reading; d', the reading through the area photometered; and d_0, the full-opaque or dark reading. Then,

$$
\begin{aligned}
D &= \log_{10} \frac{I_0}{I} \\
&= \log_{10} \frac{d - d_0}{d' - d_0} \\
&= \log_{10} (d - d_0) - \log_{10} (d' - d_0)
\end{aligned}
$$

If d and d_0 are constant, as they should be, they need be checked only infrequently and d' need be observed only on individual lines. The other readings are suppressed or implied in the reduction process in various ways.

95. Types of Microphotometers

Microphotometers may be classified under several heads:

1. Type of Illumination
   a. Projection. A considerable area of the plate is projected on a screen or field for observation and measurement.
   b. Concentrated. The light is all focused on the limited area to be measured.
2. Method of Observation
   a. Subjective. A visual match is made of the unknown and a reference density.
   b. Objective or physical. A photocell or other light-sensitive element and galvanometer eliminate personal judgment. These instruments may be either of the *null* type, in which the measuring and comparison beams are balanced against one another, or of the *deflection* type, in which the measurements may be either (*a*) read directly or (*b*) recorded automatically by photographic or graphic means.

Descriptions of a few representative instruments will illustrate the various characteristics of microphotometers and serve as a basis for some discussion of the merits and shortcomings of the various types.

Subjective microphotometers. The subjective microphotometer, although the earliest type, is today relatively little used except in special

applications.[6] In principle, such instruments are similar to the visual spectrophotometers previously described: of two beams of light from the same source, one passes through the plate to be measured and the other through some sort of variable beam weakener, such as a wedge, polarizer, or rotating sector. The two beams are brought together to form the two halves of a visual field and are matched in intensity by varying the intensity of the second beam. The process is rather slow, since a visual match requires some time, even for an experienced observer, and the scale must be read after the match. Visual matching is tiring to the operator, who can do only a limited amount without a loss of accuracy. The chief advantage of the visual microphotometer is the fact that ranges of density from low values to values as high as 8 or 10 can be covered. Such densities sometimes occur in X-ray photographs or in special applications. For most spectroscopic densitometry, however, where speed and accuracy are constantly becoming more important, the visual microphotometer has been largely supplanted by the various objective instruments.

Null-type microphotometers. Numerous null-type objective microphotometers have been built, usually employing two photocells in opposition or in a bridge circuit.[7] One beam of light, after traversing the plate under measurement, falls on one cell, while the comparison beam falls on the other cell. One beam or the other is varied by a wedge or rotating sector until the electrometer or other detector shows a balance. Essentially, these instruments replace the eye in visual balancing, and their speed is not much greater than that of subjective instruments. Their accuracy, however, is better, since it does not suffer because of fatigue on the part of the operator, and since the balancing of the two light beams minimizes the effect of changes or fluctuations in the light source. Null-type microphotometers are not so adaptable as deflection instruments to high-speed operation. An automatic-recording instrument of this type is discussed on page 265.

Deflection-type microphotometers. Perhaps the simplest objective microphotometer of the deflection type is that assembled by replacing the eyepiece of any mechanical-stage or movable-stage compound microscope with a thermopile, and by substituting for the condenser a lantern containing a lamp with a fine filament and a microscope objective. A reduced image of the lamp filament is formed on the photographic plate, which is mounted on the microscope stage. The regular microscope objective images the illuminated part of the plate on the slit before the thermopile. The slit width is adjusted to provide the desired resolu-

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[6] J. Hartmann, *Zeits. f. Instrknde*, **19**, 97, 1899.

[7] Cf. H. Rosenberg, *Zeits. f. Instrknde*, **45**, 313, 1925; also article by G. R. Harrison on densitometers and microphotometers in W. S. Forsythe, *Measurement of Radiant Energy*, p. 283. New York: McGraw-Hill Book Co., 1937.

tion; in general, the slit width should be somewhat narrower than the spectral line image on the slit. As the turning of the screw of the stage moves a line image across the slit, the galvanometer indicates, by its change in deflection, the reduction in light intensity from clear plate to line center. The line image must move slowly enough for the galvanometer to reach maximum deflection. This microphotometer is a useful expedient—satisfactory where relatively few lines are to be measured. Consideration of it shows some additional features to be sought for in a more elaborate, direct-reading instrument.

Since many of the present-day prism spectrographs of medium and large size have standardized on 4×10-inch plates, microphotometers should have a plate carriage capable of covering the full area of such a plate without the need for resetting.

It is desirable, also, that means be provided for inserting larger plates without cutting. A slide or other rapid motion should permit ready translation from point to point in any spectrum or from one spectrum to another on the plate, while a screw motion for final adjustment should be provided, together with an auxiliary slow motion to permit traversing a selected line slowly enough to ensure full deflection of the indicating instrument. It should be possible to view a considerable area of the plate at one time, perferably as an enlargement on a screen, so that any desired line may be selected and brought into position without delay. The plate carriage should provide for easy and rapid mounting and alignment of the plate, and should be placed so that the plate, the indicating scale, and the screen for observing the spectrum can be easily viewed in rapid succession without tiring movements of the eyes or head.

It should be possible to change the area of the spot measured on the plate readily and reproducibly, both in length and width. The area which can be used depends on the line width and curvature, and on the resolution required. It should be as large as is feasible, however, not only to increase the luminous energy available but also to decrease the error due to plate grain (Sec. 100). If possible, the area should be adjustable in width from about 5 to 50 microns and in length from about .5 mm to 5.0 mm.

The indicating system should be rapid and extremely stable. The galvanometer period should be not over 2 or 3 seconds. The light-sensitive element should be quick in response, free from thermal effects, and not subject to fatigue or sensitivity changes due to fluctuations in temperature or to aftereffects of illumination. The light source must be free from unsteadiness or changes in intensity to at least .1 per cent. The scale reading for the change from full opaque to clear plate with the minimum photometering area should be at least 250 scale divisions.

The Hilger non-recording photoelectric microphotometer shown in Fig. 87 embodies many of the desirable features listed above. The

fundamental similarity of this instrument to the adapted microscope-microphotometer will be apparent. The spectrogram is mounted on a stage which takes plates up to 4 × 10 inches and moves on two sets of mutually perpendicular ways so that any part of the plate is accessible. A screw, provided with a slow motion and reading to .005 mm, permits any distance up to 15 mm to be traversed very slowly.

The light from a battery-operated 18-watt bulb, after deflection by a right-angle prism, is brought to a focus by a 25-mm microscope objective which images the filament on the plate. A second objective above the
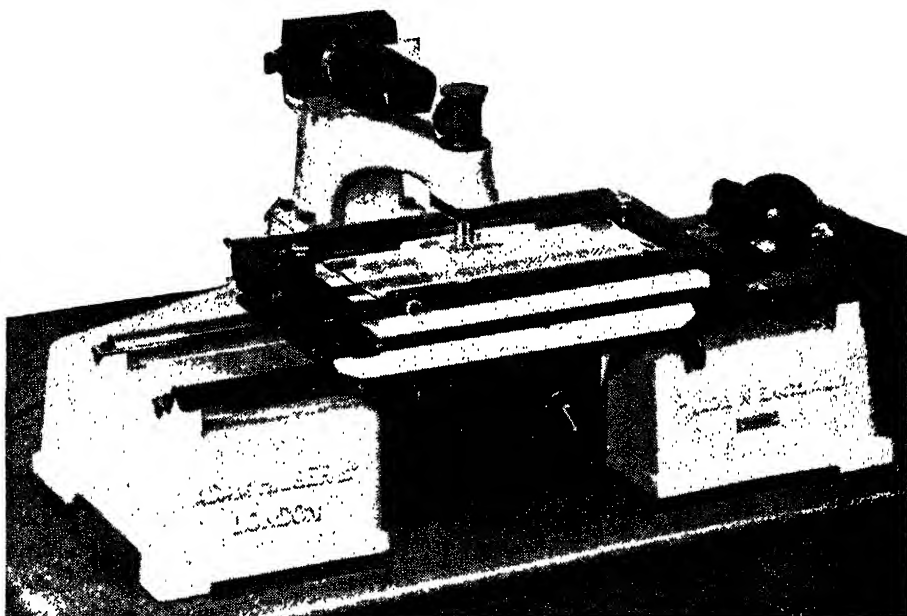
Fig. 87. Non-Recording Photoelectric Microphotometer.

stage images the beam, after another right-angle reflection, on a slit in the center of the screen above the instrument. At this point, a tenfold magnified image of the plate is formed, and since the two objectives are matched, a one-to-one image of the filament. Behind the slit, which is adjustable in .05-mm steps from .05 mm to .25 mm, is a barrier-layer cell that indicates through a galvanometer the variations in light intensity as the lines are moved across the slit. The slit width, which must be narrower than the line image, determines the resolution.

The galvanometer scale, which is not a part of the instrument, should be located for convenient viewing just above or beside the screen. The area photometered is limited in length by the illuminating system to .7 mm and can be further limited at the slit; its width is limited by the adjustable slit to $\frac{1}{10}$ the slit width. A cylindrical lens can be moved

into place between the light source and the prism to increase the length of the illuminated area to 2 mm, but, of course, with no increase in total luminous energy.   Normally, only the small area of the plate illuminated by the filament image is clearly seen on the screen. . To permit a larger area to be viewed for adjustment and identification purposes, a negative lens can be moved into the beam in place of the cylindrical lens and a larger plate area illuminated.

The photocell and slit in the Hilger microphotometer can be replaced by a unit with a slit divided horizontally into two parts, behind each of which is a photocell.   These two cells are connected in opposition and an "equalizing" lens in the light beam can be adjusted until the galvanometer reads zero on the clear plate.   The microphotometer can then be used for the spectrophotometric matching of points of the same intensity in two adjacent spectra on a plate.   The image of one spectrum is formed on the upper half of the slit and the image of the other, on the lower half; the plate is then slowly traversed until a position is found where the galvanometer reads zero.

Projection-type microphotometers.   In microphotometers of the concentrated-beam type, such as those discussed above, special provision must be made for viewing at one time more of the spectrum than the line being measured.   This complication is avoided in the projection-type instruments, where a considerable length of the spectrum is projected on a screen carrying an adjustable slit, behind which the light-sensitive element is placed.   The plate is moved on a suitable carriage with slides and slow-motion provisions, and the deflection noted as the desired lines are moved across the slit.   Instruments of this type have been marketed in the United States by the Bausch and Lomb Optical Company and by the Applied Research Laboratories of California (Fig. 88).

Projection-type microphotometers have, in general, a lower sensitivity than concentrated-beam instruments have, since the luminous energy is not concentrated in the narrow filament image but is spread over a considerable area on the plate.   If a short-period galvanometer is to be used, it is often necessary to sacrifice resolution by opening the slit in front of the photocell or by using a strong light source, with consequent troublesome problems of heat-dissipation.   An alternative is to replace the barrier-layer cell or thermocouple with a photocell and amplifier. Modern photocells are quicker in response and less subject to fatigue and temperature effects than the other detectors are, but the new difficulty of maintaining constant sensitivity and amplification is a handicap where much work is to be done.

Recording microphotometers.   When relatively few lines are to be photometered in a many-lined spectrum, and when the maximum intensity rather than the line contour is wanted, direct-reading microphotometers of the spotting type described above are more convenient and rapid

than recording instruments are. Recording instruments are generally adapted to the measurement of whole regions of the plate rather than to the measurement of individual lines. If they produce a photographic record, the plate film or paper must be processed for examination, and, finally, measurements must be made on this record. Cases often arise, however, in which it is desired to examine a large number or all of the
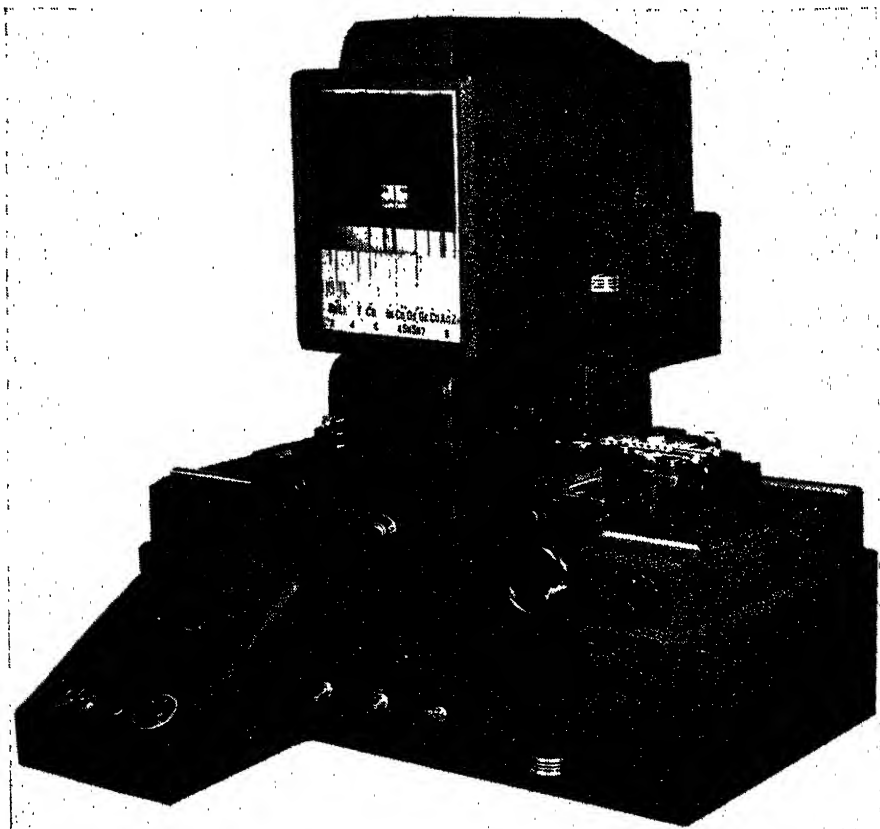
Courtesy Applied Research Laboratories and H. L. Dietert Company.

Fig. 88. Projection-Type Photoelectric Microphotometer. A comparison spectrum is projected in the lower half of the viewing field below the spectrum to be measured. The galvanometer scale is projected above the spectra.

lines on a spectrogram, or to get information about the contour of individual lines, absorption spectra, or bands, rather than to measure the maximum amplitude alone. It is then desirable and time-saving to use recording microphotometers, which make an unbroken record of the deflections of the indicating device as the spectrogram is moved continuously through the photometering light beam. Recording attachments can be combined with almost any type of deflection instrument,

a motor drive being ordinarily provided to advance the spectrogram and the record uniformly at fixed relative rates.

One of the earliest recording microphotometers to be marketed commercially was the thermoelectric instrument designed by W. J. H. Moll[8] and manufactured by Kipp and Zonen of Delft, Holland. This device has been constantly improved in speed and accuracy since its introduction, and is widely used.

The speed of operation of the Moll microphotometer is limited primarily by the response time of the vacuum thermocouple. Higher recording speeds can be attained by the substitution, as the light-sensitive element, of a vacuum-type photocell with which, unless an electrometer is employed, a vacuum-tube amplifying system must ordinarily be used to increase the small phototube currents (10^{-9} amp.). Modern phototubes have the advantages of extremely rapid response, freedom from thermal effects, low fatigue effects, and adaptability to amplifier circuits where large recording voltages are desired. The recent large commercial use of these tubes in television, wire-photo, and sound-recording applications has led to rapid improvements and developments in phototubes and amplifying circuits. In their stability and reproducibility, they are now comparable to vacuum thermocouples, while their limited spectral response has the advantage of reducing the troubles from scattered light and of making possible the use of lenses achromatized over a narrower spectral range.

A recording microphotometer, using a phototube directly connected to a quick-acting string electrometer, has been designed by Hansen[9] and is manufactured by Zeiss. The recording is done on a photographic plate. Another interesting recording instrument of this type is based on a design by Knorr and Albers[10] and is built by the Leeds and Northrup Company. It is depicted in Fig. 89. The mechanical and optical systems are essentially similar to the concentrated-beam systems previously described, and the light beam terminates in a phototube and d-c amplifier. The recording system, however, is not photographic but uses the automatic-recording potentiometer, or Speedomax recorder, of Leeds and Northrup, by means of which an inked record on a wide paper strip is obtained. The maximum amplitude of the record is 25 cm, and the speed of run can be as much as 2 mm of plate per minute. The system has the advantage that the record is immediately available without waiting for the processing of the plate or bromide paper, and can, in fact, be observed and measured while recording is going on.

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[8] W. J. H. Moll, *Proc. Phys. Soc. Lond.*, **33**, 207, 1921.
[9] G. Hansen, *Handb. d. Physik*, **78**, 570, 1925.
[10] H. V. Knorr and V. M. Albers, *Rev. Sci. Inst.*, **8**, 183, 1937; R. C. Mackler, *Proc. 7th Spec. Conf.*, p. 65.

An example of the high speeds attainable with photoelectric scanning is the automatic measuring and recording comparator-densitometer of Harrison, which has already been referred to (page 221). In this remarkable instrument, which provides at the same time automatic measure-

Fig. 89. Recording Photoelectric Microphotometer. The microphotometer unit is at the left, the Speedomax recorder at the right.

ment, reduction, and recording of wave lengths, the photometer beam activates a photocell multiplier tube. This cell, through an oscillograph, provides a continuous record of the density of the plate. By means of an electrical delay network, it also can be made to act like two cells con-

nected in opposition, whose difference current can provide a record of the density gradient of the plate. The line-wave-length recorder is also actuated by this circuit, so that the wave length of the point of zero density gradient or maximum line density is recorded. An ordinary plate can be run off with this comparator in a minute or less.

96. Homochromatic Photometry

For homochromatic photographic photometry, that is, for the determination by photographic means of either relative or absolute spectral intensities in a wave-length band so narrow that variation of plate response with wave length need not be considered, there must be provided on the same plate a series of calibration marks of known relative intensity, impressed by light of the same wave length as that to be measured. For absolute intensity determinations, the intensity at the entrance slit of the spectrograph must be known for the particular wave lengths in absolute units, such as microwatts per cm². Means for providing this information will be discussed later in connection with the topic of heterochromatic photometry (Sec. 99), that is, the determination of the relative intensities of radiations of widely differing wave length. For much spectroscopic work, however, relative intensities only are required, and their determination will be discussed first.

97. Methods of Recording Emulsion-Calibration Marks

Numerous procedures have been followed to record calibration marks on spectrograms. Simplest in principle, perhaps, is a series of timed exposures, made with a fairly wide slit and a continuous or discontinuous light source, and with the plate racked down after each exposure. This procedure embodies several weaknesses: first, the light source must remain constant and the timing must be accurate to within 1 per cent or better; second, unless it has been carefully demonstrated that the plates used follow the reciprocity law strictly, significant errors may arise from the fact that the response of the plate to time variations is different from its response to intensity variations (see Sec. 81). The reciprocity-law error can be determined and compensated for, but not easily with high precision. A preferable procedure is to vary the light intensity while permitting the marks to be impressed by times of exposure as near as possible to those of the spectra to be photometered.

With a stigmatic spectrograph, these requirements are most simply met by some arrangement for varying the light intensity along the slit or for varying the slit width with a constant light intensity. If the spectrograph with which the spectra are to be made is not stigmatic, the calibration marks may be impressed on the plate by a stigmatic instrument.

A procedure requiring no special equipment is a series of exposures to a constant source of continuous radiation, with equal exposure times, with the plate racked down after each exposure and with the slit width progressively varied in a simple geometrical ratio, say 1.5 or 2.[11]   The narrowest slit must be wide enough to ensure a diffraction pattern on the collimator lens considerably narrower than the lens, so as to prevent loss of light by diffraction (Sec. 42).   Although this method has been used and is a valuable expedient when other means are lacking, it involves certain difficulties: accuracy of timing, constancy of light source, and great accuracy in slit-width determination must be attained, and the procedure is slow and hard to reproduce exactly.[12]

Another expedient, avoiding the difficulty of fixing slit widths, is the use of the inverse-square law: a series of exposures of equal time, with a small constant source, is made at a succession of carefully measured distances from the slit; the intensities are then calculated from the inverse-square law.   Like the methods just described, this method has the weakness of using for each step a slightly different area of the optics, and it is necessary to guard against trouble from diffraction effects or optical imperfections.

Several other methods have been used for varying the intensity of the whole light beam in a known way.   One possibility, which does not appear to have been much used, is varying the temperature of an incandescent lamp for wh_   +he intensity distribution is known as a function of temperature.   Mechanical methods include the insertion in the beam of diaphragms, screens, or neutral filters.   These should be placed where the beam is of uniform cross section.   One such place is immediately before or behind the collimating lens which images the source on the spectrograph slit.   A calibrated iris diaphragm may be used, or interchangeable apertures of known size, but a rotating disc with sector openings is somewhat to be preferred because small irregularities in the uniformity of the beam are thus averaged out.   The same effect is produced by perforated screens or gauzes which when rocked are additive in effect so that two or more can be used in series.   Screens must usually be calibrated for transmission experimentally.[13]   Neutral filters can be used, but since none is strictly neutral over large wave-length ranges, they must be calibrated for transmission at the wave lengths used.   Care must be taken to see that they are uniform over their whole area, and that their faces are plane and parallel, to prevent refraction effects.   Gray glasses can be used in the visible.   In the ultraviolet, films of platinum[14]

[11] L. S. Ornstein, *Proc. Roy. Soc. Lond.*, **37**, 337, 1925.
[12] For example, P. G. Kruger, R. C. Gibbs, and R. C. Williams, *Phys. Rev.*, **41**, 322, 1932.
[13] G. R. Harrison, *J. Opt. Soc. Am.*, **18**, 492, 1929.
[14] T. R. Merton, *Proc. Roy. Soc.*, **106**, 378, 1924.

or of antimony[15] evaporated on quartz have been used down to about 2500A.

Any of the devices for weakening the intensity of the whole light beam must be used with care and judgment.   The results from methods which vary the cross section may be adversely affected by lack of uniformity of the beam at the point where the beam is interrupted.   If rotating sectors or rocking screens are used, it must be assured that fluctuations produced in the beam are not of sufficient magnitude to raise questions of intermittency effect.   If any of these methods are used over extended wave-length regions, there is a possibility that, because of lens errors or because of differential diaphragming for different wave lengths, the same results may not be produced for all wave lengths.

More convenient, faster, and easier to control than successive weakeners are methods which record all the marks simultaneously and so avoid difficulties from uncertainties in timing and source constancy.   One procedure is to replace the spectrograph slit with a stepped slit, as suggested by Duffendack[16] (Fig. 90), with a wedge-shaped slit, or with a slit head

Fig. 90.   Stepped Slit Aperture, with Opening in Logarithm Ratio of Width.

containing a number of individual slits of fixed graded widths.[17]   The steps are usually, in either case, in a geometric ratio of 1.5 or 2, and so give intensities in integral steps of logarithms to the base 1.5 or 2.

A second method of recording the marks simultaneously is to illuminate the slit with light which varies in intensity from one end of the slit to the other, either continuously or in several steps.   Several ways of securing such illumination have been devised.   A neutral wedge, a neutral step weakener, or a rotating step or logarithmic-sector disc (Fig. 91) may be placed directly in front of the slit, which must, of course, be illuminated uniformly from one end to the other.   The rotating-sector disc is subject to the objection not only that the illumination is intermittent, but also that the total time of exposure varies along the slit length, so that tests must be made to insure that errors are not introduced by intermittency effect or reciprocity-law failure.

Investigations by Webb[18] and by others have shown that intermittent exposures are satisfactory above a critical frequency which depends on

[15] Harrison, *J. Opt. Soc. Am.*, **19**, 267, 1929, credits these to Ornstein.   Details of construction in G. O. Langstroth and D. R. McRae, *Proc. 5th Summer Conf.*, p. 105.
[16] O. S. Duffendack, *J. Opt. Soc. Am.*, **23**, 101, 1933.
[17] Such multiple slits have been supplied by Kipp and Zonen, of Delft, Holland.
[18] J. H. Webb, *J. Opt. Soc. Am.*, **23**, 157 and 316, 1933.

the intensity, wave length, and emulsion. In general, it appears that each silver grain should receive, on the average, not more than one quantum per light flash. The critical speed is of the order of from 10 to 100 flashes per second under ordinary conditions, and sector-disc speeds of 1800 r. p. m. or more usually give accurate results. Recent investigations by Sawyer and Vincent have shown that not all emulsions have such
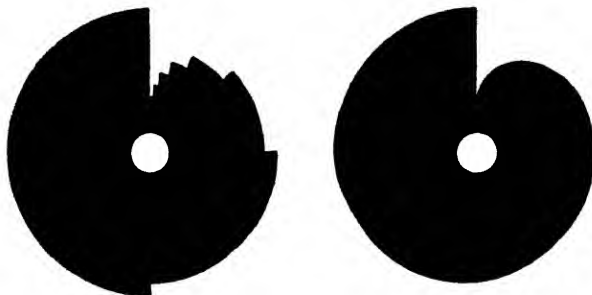
Fig. 91. Sector Discs. Stepped sector, left; logarithmic spiral sector, right.

a critical speed, and that intermittent exposures can be used only after their validity has been demonstrated for the emulsion and flash frequency used. (See page 195.)

By another method, graduated weakeners are placed close to the uniformly illuminated condenser lens and imaged by a second lens on the slit, as in Fig. 92.[19] In that case the weakener W close to the lens L_1 is uniformly illuminated. The light source S is imaged in the lens L_2 by
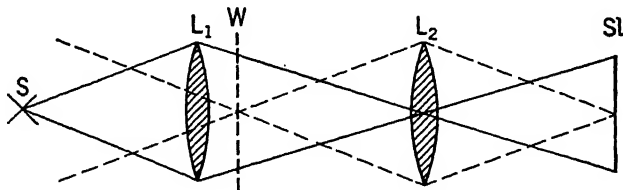
Fig. 92. Lens System for Producing Systematic Variation of Illumination along a Spectrograph Slit.

the lens L_1, while L_2 images W on the slit Sl. A third lens just before the slit may be used to image the lens L_2 and the light source on the collimator lens (see page 44), and may improve the illumination.

Simultaneous step weakening may also be attained if a uniformly illuminated step-diaphragm (Fig. 90) is imaged on the slit by a cylindrical lens. The image is then in focus along the slit, giving sharply defined strips from each slit width, which are drawn out at right angles to the slit

[19] L. S. Ornstein, W. J. H. Moll, H. C. Burger, *Objektive Spektralphotometrie*, p. 83. Braunschweig: Vieweg, 1932.

by the cylindrical lens so that the intensity of illumination is proportional to the width of the diaphragm opening. A simple arrangement of this type, originated by Hansen,[20] is shown in Fig. 93. The step-diaphragm D uniformly illuminated by the source S, which may be an integrating sphere or an opal glass, is sharply imaged on the slit Sl by the lens L in the plane of the slit (b), in which plane the cylindrical lens C has no effect. In the plane at right angles to the slit (a), the cylindrical lens draws out the image of D. On the photographic plate is then formed a set of juxtaposed continuous spectra of the source S, formed by light of intensities proportional to the various slit widths. A number of variants of this cylindrical lens arrangement have been devised or described by Kinder.[21]
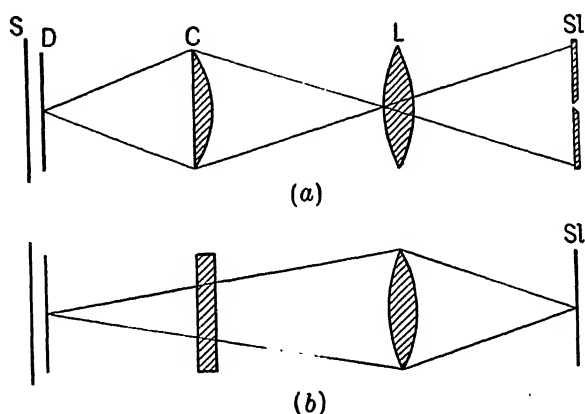
Fig. 93.   Hansen's Cylindrical Lens Arrangement for Step-Diaphragm Projection.
Section in plane at right angles to slit, (a); in plane along slit, (b).

Some of the methods of simultaneous step-weakening, as, for example, the Hansen cylinder-lens system, require special arrangements for illumination. In general, however, any source can be used which can be arranged to provide uniform illumination along the slit. For this reason, in a single-exposure calibration the source under investigation can often be used to provide self-calibration. Accordingly, with a line-spectrum source a spectrum is obtained the lines of which vary in intensity from one end to the other, either continuously or in several discrete steps. The means are then at hand for obtaining from a single line a calibration curve of the emulsion at any wave length. A serious weakness, however, is that the photometer slit must be placed along the line, with the result, in the case of continuous gradation, that, at best, only an average of the line density is obtained over the length of line covered by the slit; in the case of step gradation, there is difficulty in averaging out the grain effect

[20] G. Hansen, *Zeits. f. Physik*, **29**, 356, 1924.
[21] W. Kinder, *Zeits. f. Instrkde.*, **56**, 393, 1936.

because the length of step can hardly be more than two millimeters, which is rather short (page 271). With calibration exposures made with sources giving continuous spectra, the microphotometer slit can usually be set along the strip and a longer slit can be utilized.

Other methods of single-exposure calibration are: the use of the theoretical-intensity distribution in a single sharp spectral line as calculated from the geometry of the spectrograph;[22] the use of the theoretical relative line intensities in a line multiplet;[23] the use of any lines in a many-lined spectrum the relative intensities of which have been determined and found to be suitable and constant.[24] These methods, however, must be used with extreme care. In the case of the last two, particularly, it must be ascertained experimentally that the source used reproduces the lines in question with great constancy in relative intensity.

Of the methods of the last paragraph, only those which utilize the intrinsic shape or relative intensities of spectral lines can be applied, without precautions, to astigmatic as well as to stigmatic spectrographs. Those which utilize the successive recording of spectra of different graded intensities can be used if the line-image length is limited by diaphragms before the slit or by some other means that will prevent overlapping of lines. The methods which produce gradual or step weakening of the light along the slit can be modified to produce this effect at the vertical image point instead (page 76). Frerichs[25] has pointed out how a step weakener, rotating sector, or other similar device may be placed at this focal point of the concave grating (page 130). The theoretical variation of line intensity along a line, due to the astigmatic drawing out of the line by a concave grating (page 129), provides another method of calibrating the plate emulsion.[26] The astigmatism of the spectrograph is in one sense an advantage, for, since points on the slit are drawn out into a line in the image, the effect of small irregularities in the slit, in the optics, or in uniformity of illumination may be averaged out.

98. The Determination and Use of Characteristic Curves

From microphotometer readings taken at any wave length from a set of calibration marks obtained in any of the ways mentioned, an emulsion-characteristic curve may be drawn for that wave length. If desired, density,

$$D = \log_{10} \frac{d - d_0}{d' - d_0}$$

[22] L. S. Ornstein and M. Minnaert, *Zeits. f. Physik*, **43**, 404, 1927.
[23] G. R. Harrison, *J. Opt. Soc. Am.*, **19**, 267, 1929.
[24] H. B. Vincent and R. A. Sawyer, *J. App. Phys.*, **8**, 163, 1937.
[25] R. Frerichs, *Zeits. f. Physik*, **36**, 524, 1926.
[26] G. H. Dieke, *J. Opt. Soc. Am.*, **23**, 280, 1933; Sister M. I. Bresch, *J. Opt. Soc. Am.*, **28**, 493, 1938.

(page 249), may be calculated from the readings, and H and D curves of D against $\log_{10} I$ plotted. For most purposes, however, it is sufficient and simpler to plot some functions of these quantities obtainable without reduction of data. One procedure is to adjust the intensity of the microphotometer light source before readings are taken, so that the clear-plate reading, d, is exactly 100; the full-opaque reading, d_0, is, of course, zero, and $D = \log_{10}(100/d')$. Moreover, if galvanometer deflections are plotted against numbers proportional to the intensity of the various calibration steps on log-log paper, an inverse cali-

Fig. 94. Inverse Calibration Curve, on Logarithmic Scale, of Galvanometer Deflection versus Relative Intensity.

bration curve (Fig. 94) is obtained from which the intensities corresponding to any galvanometer deflections can be read. If, as is usual, the geometrical ratio of the intensity steps is in the neighborhood of 1.5 or 2.0, the intensity logarithm will be to the base of this ratio rather than to the base 10.
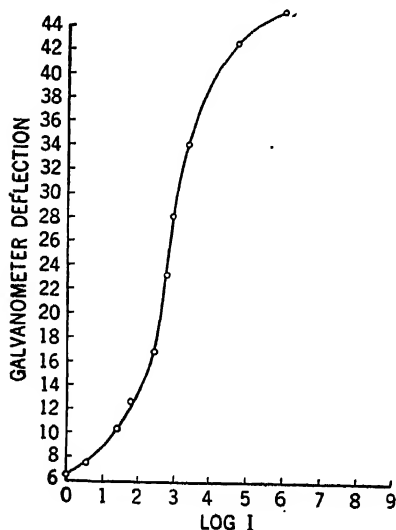
Fig. 95. Calibration Curve, on Logarithmic Scale, of Reversed Galvanometer Deflection versus Relative Intensity.

Another way of making microphotometer readings is to reverse the galvanometer scale so that the dark, or full-opaque, reading is a maximum and the clear-plate reading a minimum, say 500 and 0, respectively, or any other arbitrary values. This arrangement has the advantage that blacker lines give larger readings, which seems to many observers more logical. If galvanometer readings and intensity factors are then plotted on log-log paper, a curve is obtained which resembles an H and D curve and which is as useful for reading intensities. Or, since the intensity steps used in calibration usually have a simple integral ratio, the log I values to this base are successive integers. If, then, galvanometer deflec-

tions are plotted against log I on ordinary co-ordinate paper, again a curve similar to the H and D curve is obtained, but usually with a shorter straight portion (Fig. 95). This curve is sometimes preferred because of somewhat greater ease in plotting.

It often happens in the case of single-exposure calibration that the five to seven points obtained are not sufficient for plotting the whole curve. In that case, points from two exposures, giving overlapping blackening, can be plotted on the same sheet, if the curves are shifted laterally until the overlapping parts coincide. The two exposures should, of course, be made with the same exposure times; the source intensities in the two cases can be varied by any of the methods previously discussed. The satisfactory overlapping of two such partial curves is an indication of self-consistency in the calibration procedure, and is, in fact, one of the best checks on the accuracy of the calibration method used.

The intensity, as read from any form of calibration curve, is given in arbitrary units and depends fundamentally on the position of the zero of the intensity scale, which is not always fixed. However, for much photometric work relative rather than absolute intensities are wanted. Since $\log (I_1/I_2) = \log I_1 - \log I_2 = (KX_1 - A) - (KX_2 - A)$, it is clear that, by taking the difference of two abscissae from the graph, $\log (I_1/I_2)$ is obtained immediately, and, since A cancels, without any question of the position of the origin.

Strictly speaking, determination of intensities from a single calibration curve is valid only over a spectral range in which both plate contrast and plate sensitivity are constant. In spectrochemical work these ranges are sometimes exceeded because, under constant experimental conditions, the uncorrected intensity ratio of two lines differing considerably in wave length may still be significant of the concentration of the element responsible for one of the lines.

It is possible, if the utmost precision is not required, to arrange attachments to recording microphotometers to give direct registration of intensity rather than of plate blackening. Minnaert and Houtgast[27] have devised an attachment for the Moll microphotometer to convert blackening into intensity. The impulse from the vacuum thermocouple of the microphotometer goes to an auxiliary galvanometer, the mirror of which reflects a vertical line of light on a diaphragm. This diaphragm is cut in the shape of the I-D curve of the emulsion. The position to which the vertical line of light is deflected along this diaphragm by the galvanometer is proportional to D; and the length of the line—and therefore the quantity of light passing through the diaphragm—is proportional to I, the light intensity producing this D. The light passing through the diaphragm is collected by a lens on a photocell that is connected to the

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[27] M. Minnaert and J. Houtgast, *Zeits. f. Astrophysik*, **15**, 354, 1938.

recording galvanometer of the Moll microphotometer, which then records *I* directly.   Since an *I-D* curve can hold for a limited spectral range only, any one diaphragm is good only for a range for which a constant *I-D* curve can be assumed, and must be replaced by another to extend the range.

This difficulty of limited range is met by a recording microphotometer of Williams and Hiltner.[28]   This ingenious device balances a light beam which has traversed the spectrum against one which has passed through the corresponding wave length on a set of continuous intensity marks recorded with a logarithmic-sector disc or logarithmic-wedge slit on another piece of the same plate.   The intensity marks are displaced sideways until the two beams balance—the impulse coming from the amount of inequality in the two beams—and an optical lever records the displacement, which is proportional to intensity.   The original paper
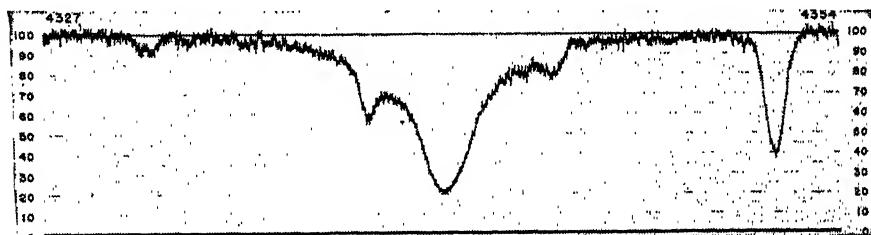
Fig. 96.   Tracing Made with Williams-Hiltner Microphotometer of Intensity Variation near H_γ (center) in the Spectrum of α Cygni.

should be consulted for the details of this instrument.   In its original form, the accuracy of the device is limited by the small area of the light beam; this area, however, can be increased, since it was fixed by the stellar spectra to be investigated and not by the principle of the design. A tracing made with this instrument, of the H_γ region of the spectrum of α Cygni, is shown in Fig. 96.

99. Heterochromatic Photometry

In general, over appreciable ranges of wave length—even as small a range as 20A—it will be found that the apparent relative intensities of two separated wave lengths are a function both of the photographic emulsion and of the spectrograph used.   The sensitivity of the emulsion (the reciprocal of the light intensity required to produce unit density in unit time) is a function of wave length, and so also is the contrast, or slope, of the characteristic curve.   With some emulsions, these two functions change relatively slowly over considerable ranges, but with other

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[28] R. C. Williams and A. Hiltner, *Publ. Am. Astr. Soc.*, **10**, 33, 1939.

emulsions, and with all near the ends of the sensitivity range, variation may be very rapid.

The apparent intensity recorded on the plate is affected by loss of light by absorption and by reflection in its passage through the spectrograph. It is also affected by numerous other factors which likewise vary with wave length, such as dispersion, astigmatism, focal length of the lenses, plate tilt, and size of limiting aperture. All of these causes affect the intensity of continuous spectra, and if they affect the width of the slit image formed on the plate, they will affect the intensity of line spectra also. Methods for the correction of most of these effects by calculation have been discussed elsewhere (Sec. 43).

While it is possible to correlate intensity determinations at different wave lengths by applying corrections for the emulsion and instrument effects mentioned above, it is generally preferable to make all these corrections experimentally by the use of a light source of known energy distribution. The spectrum of this source is photographed on the same plate with the spectrum to be photometered, and may, if convenient, also be used to provide the calibration marks. By means of the usual calibration curve for each wave length, the unknown densities are determined in terms of the density of the standard source at that wave length. The known energy distribution of the standard source is then used to relate, by interpolation, the intensities at the different wave lengths.

Various types of standard sources are available. The simplest in principle is the black body, which is useful throughout the infrared, visible, and near ultraviolet regions. Its energy distribution can be calculated from a knowledge of its temperature (page 18). Numerous authors have described the construction of black-body sources.[29] Calibrated tungsten lamps are, in general, the most convenient and practical for general use. Some manufacturers, as, for example, Kipp and Zonen, supply ribbon-filament lamps with either relative or absolute calibration of the amount of energy emitted at any particular wave length. Various standardizing laboratories, such as the various government laboratories, are prepared to standardize such lamps, and Ornstein and his associates[30] have described methods for the calibration of standard lamps. Heterochromatic photographic photometry in the region below the range of these incandescent sources (about 2500A) is not at present entirely satisfactory. Although some pioneer work has been done,[31] difficulties with photographic materials, the lack of entirely satisfactory light

[29] E. P. Hyde and W. E. Forsythe, *Astrophys. J.*, **51**, 244, 1920; H. B. Dorgelo, *Phys. Zeit.*, **26**, 767, 1925.

[30] *Objektive Spektral-photometrie*, p. 102; L. S. Ornstein, D. Vermeulen, and E. F. M. van der Held, *J. Opt. Soc. Am.*, **20**, 573, 1930.

[31] G. R. Harrison and P. A. Leighton, *J. Opt. Soc. Am.*, **20**, 313, 1930; R. Montague and R. Picard, *Compt. Rend.*, **202**, 477, 1936.

sources, and the problems of vacuum technique below 2000A render results in this region less satisfactory than at longer wave lengths.

If the standard lamp used has an absolute calibration, giving, under fixed conditions and at a given distance from the lamp, the energy at each wave length in absolute units, such as microwatts per square centimeter, heterochromatic photometric determinations can be made directly in absolute rather than relative units. The photometric comparison gives at once the energy which is incident on the slit at each wave length. If the relative energy distribution only of the lamp source is known, and if a second lamp is available for which the total energy radiated is known, the problem can be solved in absolute units. Such lamps are somewhat cheaper and more readily obtainable than those with absolute, distributed calibration. With the help of filters of calibrated transmission and of a nonselective receiver of radiation, such as a thermopile and galvanometer, the lamp of known total radiation can be used to make an absolute calibration of the source of known relative distribution. The procedure, while requiring care, is relatively simple and, because of its specialized nature, will not be described in detail here.[32]

100. Notes on Photographic-Microphotometric Practice

Numerous procedures have been described above for recording calibration marks on photographic plates. The choice of a method in a particular case depends, to a large extent, on the equipment available and on the problem at hand. It may be noted that some of the methods involve, for the different calibration steps, the use of different parts of the optical system of the spectrograph; some introduce possibilities of errors due to diffraction effects, stray and scattered light, intermittency effect, reciprocity failure of the photographic emulsion, or dust or scratches on the optics; and all require careful measurements, direct or implied, of time or distance. It may be found that because of some of these, or other, errors, the calibration method used gives calibration curves which are not quite smooth, or that the results, while consistent in themselves, do not agree with those obtained by other observers or with other instruments. If the results are to be absolute rather than relative, and especially if they are to be comparable with those of other observers, it is highly desirable to use, as checks on each other, two methods of calibration as widely different in principle as possible. Simultaneous stepweakening methods and self-calibrations by the source under experiment are to be preferred.

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[32] See for example, W. W. Coblentz, R. Stair, and J. M. Hogue, *U.S. Bur. of Stand. J. of Res.*, **7**, 723, 1931.

If the source under investigation cannot itself be used for the plate calibration, a source similar in character is desirable. Difficulties from intermittency effect or reciprocity-law failures are then diminished. Thus, for spark work, a source of the same frequency as that to be studied should be used; similar intensities in the two sources will make exposures for the same time possible. If for photometry of continuous spectra continuous sources are used for calibration, and if for photometry of line-spectra line sources are used, errors due to source background, scattered light, and Eberhard effect of the photographic emulsion will be much reduced because of the similarity of the spectra. The calibration light source must cover the range being studied and must emit radiations of suitable intensity at the wave lengths under examination. It should be as constant and reproducible as possible; incandescent lamps, discharge tubes, and controlled sparks are preferable to open arcs or flames.

The ideal spectrograph for photographic photometry would include among its features adequate dispersion for the use of slits at least 50μ wide, a minimum of stray- and scattered-light contribution to the spectrum background, a slit five to ten millimeters long, and line-image curvature, if any, so small that at least five millimeters of line can be photometered. The minimum necessary dispersion depends upon the spectrum to be examined; for the complex spectra of heavy metals or of bands, grating or prism spectrographs with a dispersion of 5 angstroms per mm or more are needed, while smaller instruments have adequate dispersion for simple spectra. If, however, the source is a line source which emits considerable continuous background light, a large dispersion spreads out and reduces the intensity of the background relative to that of the lines, although at the expense of the range covered on a plate and, usually, at the expense of the illumination. A certain amount of stray and scattered light will be found in any spectrograph; for photometric work, every effort should be made to reduce this false light as much as possible. Scattered light is worse in a poor grating than in a prism instrument, since to a greater or less degree, light is always scattered from irregularities in the grating grooves and from scratches. The best grating spectrographs show less scattered light than prism types; they have fewer surfaces to reflect and scatter the light. Although reflected light is likely to be worse in a Littrow-type prism instrument than in a straight-through type, care in design and adjustment can help greatly. Furthermore, since wide slits are usually used and the best definition is not vital, the lens can be tilted, if necessary, to throw reflections off the plate.

The slit, for continuous spectra, should be as narrow as is consistent with sufficient intensity. For line spectra, if the photometric record or close individual readings in a non-recording instrument are to reveal the line shape, the slit must be near the critical slit width. For most line

photometry, however, the lines are of reasonably similar shape, and a single reading of the maximum density is assumed to be proportional to the line intensity. The slit should be several times the critical slit width, and wide enough to give a flat-topped line image somewhat wider than the microphotometer slit. In general, a slit width of 30–60μ satisfies all these requirements and gives a line area sufficiently large so that the plate-grain errors are minimized.

Almost any photographic plate or film and almost any developer can be used for photometric work, although all are not equally suitable. Fast emulsions ordinarily show a greater tendency to chemical fog or background, more graininess, and lower contrast than slower plates—all factors which limit accuracy. On the other hand, emulsions of high contrast, while sensitive to small changes in exposure, limit the usable range of exposure and may, because of high inertia, unduly extend the exposure time. Dyed and ultraviolet sensitized plates and films are, in general, to be avoided except in the regions which require their use. Dyes, unless fully washed out in processing, may add appreciably to the clear-plate background; ultraviolet sensitizers are likely to affect the uniformity and graininess of the emulsion adversely.

The developer should give uniform action without chemical fog, staining of the emulsion, or the production of large grain size. In general, contrast increases with concentration of developer and time of development and varies with the formula used. (See Sec. 82.) Potassium bromide decreases contrast. Rodinal and various elon-hydrochinon formulae, which have been widely used in photometry, give moderate grain size, small Eberhard effect, and little chemical fog. Glycine gives low contrast. Pyro tends to discolor the emulsion. Caustic-hydroquinone developers are very rapid and give high contrast; they have been used in quantitative spectrochemistry where high speed and precision are required, but the contraction effects produced by this developer make its use inadvisable where accurate position measurement is required.[33]

To secure uniform development, rocking or, better, brushing, is desirable during development. Machine development is probably best, and Bloch and Horton and others have described machines that can be used.[34] Vincent and Sawyer have described a simple rocking-tray arrangement which is adequate for most purposes.[35] The plates should be hardened with a good hardener, such as chrome alum or formalin. After being fixed and washed, the plates should be swabbed on both sides with the edge of the hand, a tuft of wet cotton, or a moist viscose sponge, to remove "bloom" and excess water. Whether drying is done in free air or, for

[33] L. S. Ornstein and M. Minnaert, *Zeits. f. Physik*, **43**, 409, 1927.

[34] O. Bloch and H. Horton, *Phot. Journ.*, **68**, 352, 1928; also Dobson, Griffith, and Harrison, *Photographic Photometry*, p. 121.

[35] H. B. Vincent and R. A. Sawyer, *Spectrochim Acta*, **1**, 131, 1939.

the sake of speed, over heating coils with a fan to remove the moist air, care must be taken to avoid dust and mars.

In microphotometering the plate or film, the photometering light beam or slit which limits the width of the area scanned in the spectrum should be narrower than the flat-topped portion of the spectral lines. In general, this means that the effective width on the plate must be from one-half to two-thirds the width of the spectrograph slit. If the microphotometer is of the hand-operated, non-recording type, the plate motion must move the line across the light beam slowly enough for the deflection instrument to reach its maximum reading. The speed depends, of course, on the period of the recording instrument. As a rough guide, it will be found satisfactory if the light beam is moved along the plate a distance equal to the spectrograph slit width in a time slightly more than the full period of the recorder. Thus, with a 60μ spectrograph slit and a 30μ light beam, a full deflection on a galvanometer of two-second period will be attained if three seconds are taken for the beam to cross a line at a uniform rate. A slow motion should be provided so that the beam can cross the line at this rate without the need for great delicacy or extreme slowness of hand motion. Where much reading is to be done, a uniform traverse of the beam is much to be preferred to a fixed setting at the point of maximum density. The speed is much better and the strain of operating much less.

In industrial production, where perhaps hundreds of lines are read in a day, a motor drive engaged by an electrically operated clutch of some kind is a valuable aid. As in the case of recording instruments, it is not necessary that the motion be quite so slow as in hand operation, since it can be assured that the speed, which is always the same, will be the optimum time. The problem has been discussed by Ornstein and van Kreveld,[36] who have pointed out that the galvanometer should follow as quickly as possible the macroscopic deviations of the light-sensitive device, while indicating as little as possible of the microscopic deviations caused by graininess. They state that a critically damped galvanometer is better than an over-damped one, since the initial velocity is less for the same time of indication, and they cite a Moll microphotometer with a critically damped galvanometer of $2\pi/30$-second period. The time of indication will be $\frac{1}{30}$ second. The plate velocity is 33μ per second, and the narrowest beam of 2μ then covers its own width in $\frac{1}{16}$ second—a condition favorable, according to their theory, to the suppression of grain.

Graininess is evidenced in a microphotometer record by small, irregular peaks in the trace of the plate background or of the flat-top of lines (see Fig. 74). These fluctuations, of course, affect the recorded heights of sharp lines in a purely random way.[37] In the case of a manual setting

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[36] L. S. Ornstein and A. van Kreveld, *Physica*, **3**, 815, 1936.

[37] A. van Kreveld, *J. Opt. Soc. Am.*, **26**, 170, 1936, has shown that the graininess fluctuations in the record follow a pure Gauss frequency law.

on a line, the readings will vary for slightly different settings because of variation in the number of grains included in the light beam. The resulting error will be reduced by the use of finer-grained emulsions and of larger light-beam areas, since the graininess error should be closely proportional to the square root of the number of grains in the area. Some observations on this point have been published by Kaiser,[38] who determined the error due to the emulsion in photometric measurements after the elimination of errors due to the photometer or light source. He found, with spectral lines 1 mm long and a slit width of 0.1 mm on densities from 0.3 to 1.6, a standard deviation in density of 0.85 per cent with *reproduktionsplatte* (process plates), and of 1.43 per cent with *silbereosinplatte* (silver-eosin plates). When the slit width with the silver-eosin plates was decreased to 0.02 mm, the error rose to 2.0 per cent. Some measurements at the University of Michigan[39] gave for Cramer contrast plates a standard deviation of 1.74 per cent with a slit 0.7 mm long and 10μ wide, while with a 25μ slit the error fell to 0.85 per cent. For Eastman Kodalith plates, with a slit $0.7 \times 10\mu$, the standard deviation was 0.97 per cent. It is clear that the quoted errors include those due not only to graininess of the plate, but also to variations in sensitivity and thickness of the emulsion. The plate errors may apparently be held to much smaller values than those sometimes quoted. They are diminished by using finer-grained plates and by using larger photometer-beam areas. Since the error decreased in these measurements roughly with the square root of the area, it appears that with larger areas, say $3\text{-}5$ mm $\times 50\mu$, the error might be reduced to 0.5 per cent, or less. Plate errors of 3 to 5 per cent, sometimes mentioned in the older literature as possible, should not occur with modern emulsions and plate-production control when good processing technique and emulsions of good contrast and reasonably fine grain are used.

The readings used in calculating density are the "clear plate" reading, the "dark" or "zero" reading, and the reading for the plate region or line investigated (see page 262). The dark reading is taken by swinging the sensitive element out of the beam or by interrupting the beam with a shutter. Care must be taken, in either case, to make sure that stray radiation does not enter the cell and cause a false reading. For this reason the shutter is usually best placed between the light source and the plate. Because of grain, background, or variations in emulsion thickness and sensitivity, the clear-plate reading d will vary with the portion of clear plate used. While an average value for several points can be taken, it is usually as satisfactory to choose arbitrarily a uniform and clear spot for the clear-plate reading. Furthermore, if, as is often the

[38] H. Kaiser, *Zeits. f. Techn. Phys.*, **17**, 227, 1936.

[39] H. B. Vincent and R. A. Sawyer, *J. Opt. Soc. Am.*, **31**, 639, 1941.

case, relative rather than absolute values of density or intensity are wanted, the exact values of d and d_0 are not vital. It is vital, however, that the values of d and d_0 be frequently checked and that they remain constant.

Practically all microphotometers require a preliminary warm-up period, and, until the light source and detector system reach equilibrium, there will be some drift of the zero reading and some instability of sensitivity. A steady condition should be reached in a reasonable time—usually, an hour or less. Difficulty thereafter may arise from temperature, thermoelectric, or fatigue effects on the detecting system, all types of which are subject to some or all of these troubles to a greater or less degree. The commercial application of light-sensitive elements, as in sound recording and photograph transmission, has led to rapid improvements in the field in recent years. Careful testing of the system used is advisable, however. Fluctuations in the light source are always a potential source of difficulty.

The usual light source is an incandescent filament in a vacuum or gas-filled envelope; and since, for such lamps, the luminous output varies for small voltage changes about ten times as fast as the voltage, it is necessary to have extremely good control of voltage—to at least one-tenth of 1 per cent. Resonant-type voltage control of alternating-current supply is likely to be inadequate, especially in industrial plants, because of the failure of these devices to respond to small fluctuations in frequency. Small lamps operated by storage battery are generally satisfactory. If the instrument is to be used for many hours a day, it may be necessary to provide trickle-charging for the storage battery and, if extreme precision is demanded, some form of voltage control.[40]

The readings made with the microphotometer may need to be corrected for background in the spectrum. While every effort should be made to reduce background, there is a certain amount in every spectrum. In line spectra it may appear from continuous radiation in the light source, from incandescent particles, or from unresolved bands. In both line and continuous spectra, some background comes from scattered or reflected stray light in the spectrograph. This may affect the readings even if it does not produce a visible effect between the lines. Light below the inertia level of intensity falling on the plate, and thus of itself producing no visible effect, will be added to the spectral line radiation and increase its apparent intensity. Visible background may be corrected for by making a microphotometer reading of the background, converting the galvanometer deflection to intensity, and subtracting the background intensity from the line intensity. The assumption is that the background

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[40] R. A. Sawyer and H. B. Vincent, *Proc. 5th Summer Conf. on Spec., 1937*, p. 1. New York; J. Wiley and Sons, 1938.

intensity under the line is the same as that in the immediate neighborhood where the background reading is taken. This assumption is ordinarily justified; but in cases where the correction for background intensity is 10 per cent or more, too much confidence should not be placed in the precision of the results.

It was observed by Schwarzschild and Villiger[41] that if the illuminated area of the plate was larger than the line area being photometered, false light scattered by the silver grains or reflected from the lens surfaces could be thrown into the light-sensitive element and could make the line blackening appear too small. Less difficulty from this source arises in instruments in which a fore-slit limits the illuminated area to that photometered. In most non-recording instruments a considerably larger area is illuminated and projected on a screen, and error from this Schwarzschild-Villiger effect is likely. It is advisable to test for the presence of this error in any case, since it leads to a variable error which depends upon the density of the region surrounding the area photometered.

The effect has been studied by Keck,[42] who has given a simple test for it. Keck points out that false light may arise from at least four causes: (1) from the objective which images the plate on the light-sensitive cell—because of lens aberrations, multiple reflections at inner lens surfaces, or diffraction at the lens margins; (2) from scattering by dust particles on any surfaces between the plate and the cell; (3) from reflection from the lens back onto the area measured on the plate; (4) from multiple reflections in glass cover-plate (if such is used to hold a film, for example).

Fig. 97. Arrangement Used by Keck for Measurement of False Light in Microphotometer.

Keck determined the amount of the error due to stray light by replacing the photographic plate with a movable, sharp, single-slit jaw. Beginning at the optic axis, this jaw was moved by a measurable amount x to cut off more and more of the field, and the amount of light reaching the cell was observed. The set-up is shown diagrammatically in Fig. 97. For x larger than half the projected width on the focal plane of the slit, only scattered light enters the cell. Typical data taken by Keck on a

[41] K. Schwarzschild and W. Villiger, *Astrophys. J.*, **23**, 287, 1906.

[42] P. H. Keck, *Zeiss-Nachrichten*, **10**, 24, 1936, reprinted as *Zeiss Bulletin, Mess* 765.

Zeiss recording microphotometer are shown in Fig. 98, where curve *1* is for a jaw with upper surface blackened; *2*, for a jaw with upper surface polished; and *3*, for a blackened jaw covered with a cover glass.   Since the effect is 1 per cent, or less, of the normal reading, a recording device more sensitive than the normal one is required.   The large difference between curves *1* and *2*, with blackened and polished top, respectively, for the slit jaw, shows that a considerable effect is due to light reflected back from the objective.   The curves are, of course, integral curves; that is, they give at any point the effect due to all stray light from points outside that jaw setting.   By moving a narrow slit instead of a single jaw across the field, Keck measured the stray-light effect from narrow zones.   The results, when integrated, are consistent with the single-jaw
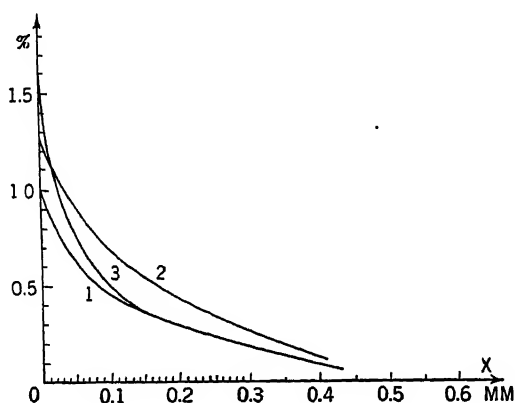
Fig. 98.   Stray-Light Measurements by Keck.

data, but are more difficult to get because of the smaller readings and give little new information.

Since it is desirable in non-recording microphotometers to illuminate a considerable plate area, it is generally necessary to take steps to reduce stray light.   Effects from the objective lens can be reduced by using better-corrected lenses and so decreasing image spreading due to aberrations; by reducing reflections from lens surfaces, through careful design of lens curvatures and through coating surfaces with lithium fluoride films (see page 113); and by reducing diffraction effects, by filling the objective lens incompletely with the light beam.   Scattering due to dust particles is easily reduced to a negligible amount by keeping the lenses reasonably clean.   Stray light arising from light passing through the plate areas outside the slit area can be greatly reduced by the use of a fore-slit of colored filter glass of a color to which the cell is insensitive but which is easily visible.[43]   Red, yellow, and green glasses have been

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[43] G. R. Harrison, *Rev. Sci. Instr.*, **25**, 169, 1935; F. Goos and P. P. Koch, *Zeits. f. Physik*, **44**, 855, 1922.

thus used.   Finally, correction can be made for the error due to the remaining false light.   Keck shows how this correction can be made, and his results indicate that, if absolute intensity values of good precision are wanted at high densities, it may be important.

101. Errors in Photographic Photometry

The errors arising in microphotometric determination of intensities which have been discussed are of two kinds: accidental or indeterminate errors of observation, and systematic or determinate errors of equipment and method.   The systematic errors arise from such causes as stray light in the microphotometer, zero drift or sensitivity change in the measuring system, plate background due to chemical fog, stray light in the spectrograph or from the light source, intermittency or reciprocity effects in the emulsion used, and faulty methods or standards in the calibration patterns.   Methods of testing for and evaluating most of these errors have been discussed.   Every attempt should be made to determine and eliminate such errors, or, if elimination is not feasible, to evaluate and correct for their effects.[44]

The causes of accidental errors, apart from fluctuations in the light source, which are not strictly photometric errors, are chiefly of two kinds: plate errors and measurement errors.   These are random errors. They arise in the plate from grain, and from variations in emulsion thickness and sensitivity, in temperature, in solution concentration, and in processing techniques.   The plate errors will be greater if the points whose densities are to be compared are far apart on the plate, especially if one of the points is near one edge of the plate.   Random errors in measurement arise from such causes as the jarring of the galvanometer, erratic fluctuations of light-source intensity, and uncertainty in estimating the scale reading.

The random or accidental errors cannot be wholly eliminated.   They can be reduced in importance by careful design, and by choice of instruments and techniques.   If the sources of random error are numerous enough and truly governed by chance in sign and magnitude, they will follow a Gaussian distribution.   Their magnitude may then be calculated from the mean of a considerable number of observations.   The standard deviation is given by

$$\sigma = \sqrt{\frac{\Sigma d^2}{n-1}}$$

where Σd^2 is the sum of the squares of the deviations from the mean of the individual results, and n the number of observations.   In a Gauss distribution, 67 per cent of the results should deviate from the mean by not more than this amount.   In a particular case, the value observed

[44] R. A. Sawyer and H. B. Vincent, *J. Opt. Soc. Am.*, **31**, 47, 1941; **32**, 686, 1942.

for percentage error of measurement will depend on the magnitude measured, since the relative uncertainty will decrease, up to a point, with the size of the quantity observed.   Kaiser,[45] in repeated measurement of the same spot on a plate with a Zeiss non-recording microphotometer for a density of 1.0, corresponding to a scale reading of 500 mm, obtained 0.0003 as the standard deviation in density.   This is an extremely favorable case, but in general, the measurement errors should be less than the plate errors.   Some data on plate error have already been given (page 271) showing that, at densities in the ordinary range from 0.3 to 1.6, a mean plate error of from 0.5 to 2.0 per cent may be attained.

The errors quoted are those to be expected in a single observation. If the mean of several observations is taken, the error of the mean is reduced in the ratio of the square root of the number of observations. It is hardly justifiable to go beyond 8 or 10 observations; at that number, the error is reduced to one-third that of a single observation, and photometric accuracy of 1 per cent or better in the determination of intensity is then readily reached.   While this accuracy is not so good as that attained in some other types of measurement, it is adequate for most present-day spectroscopic work, since the fluctuations to be expected in practically all discharge-type light sources are at least of this order, and often greater.

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    bibliography.
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    Braunschweig: Vieweg, 1932.

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[45] Ref. 38, p. 271.

CHAPTER 11

Apparatus and Methods of Infrared Spectroscopy

Strictly speaking, the infrared region is all that part of the spectrum of longer wave length than the red end of the visible spectrum, that is, beyond about 7,000A. The use of photography in spectroscopy, however, shifted the criterion for the definition of the "infrared" from the limit of sensitivity of the human eye to that of the photographic emulsion. Recent developments in infrared photography have extended to at least 12,000A the region to which the ordinary photographic techniques are applicable. The infrared region, then, is now understood to be that to which special methods must be applied, and extends from this photographic limit to the longest wave lengths yet measured optically, about 500μ (500,000A).

102. Infrared Methods

The methods used in the investigation of the infrared radiation, which is also known as heat radiation, are essentially the methods of spectroradiometry. The instruments used, although often called spectrometers or spectrographs, are essentially monochromators or spectroradiometers; that is, they are arranged to measure directly the intensity of the radiation that is focused, line by line or by short wave-length regions, upon their detecting device, which is usually placed behind an exit slit. Infrared spectroradiometers differ from those used in the ultraviolet, or visible, regions chiefly because of the optical characteristics of the infrared region.

Most important of these characteristics is the limited range of transparency in the infrared of most optical materials. Glass prisms and lenses are usable only to wave lengths of about 2.5μ. Beyond this point crystals of the various alkali halides are satisfactory, each, however, for a limited region (see page 69). Above 28μ no material sufficiently transparent for optical use is known, and gratings must be used as dispersing agents.

The lack of optical materials of a wide range of transparency has led to the use of mirrors in place of lenses in infrared spectroradiometers, and their use has some advantages. For mirrors, several of the metals that have a uniformly high reflecting power throughout the whole region are used. Gold or silver deposited on glass is most commonly employed. Furthermore, mirrors are free from chromatic aberration. Although

concave mirrors can be used only on or near their axes, because of their spherical aberration and astigmatism, this limitation is not a serious drawback in a spectroradiometer, where no extended spectral range is examined at one setting.

The detectors of radiation used in infrared spectroscopes may be of any types sensitive to heat radiation. They are generally of the non-selective type, such as the blackened-vane radiometer, radiomicrometer, bolometer, or the thermopile and galvanometer. Although all of these instruments have been used for infrared detection and measurement, in recent years the thermopile and galvanometer have almost wholly displaced the other detectors. The present superiority of this combination is due to the development of the vacuum thermopile, the perfection of amplifying devices for the galvanometer, and the greater convenience of mounting and using the galvanometer.

103. Infrared Spectrographs

The spectrographs used in the infrared fall into three main classes, depending on the type of dispersing agent: prism, grating, or combination prism-grating instruments. Although some variety of arrangements are used, nearly all are of the Littrow-type, in which the beam, after dispersion, retraces its path, in part at least, using again the same mirror system.

Although some infrared spectrometers have been placed on the market by manufacturers, commercial developments in this field have been limited by the fact that the number of workers in the infrared have always been much fewer than in the photographic field. The available instruments have been, for the most part, rather small, and most workers have preferred to design and set up their own. Recent interest in industrial applications of the infrared absorption spectrum, however, may lead to the commercial production of more powerful equipment.

104. Prism Spectrometers

Prism instruments are used in the near infrared mainly in cases where brilliance of spectrum rather than high resolving power is desired, and where the spectra to be examined are not too complicated. With most prism instruments, it has not been possible to attain a resolving power that will separate lines that are closer than about 10 cm^{-1}.[1] The limitation results from the small size of the available crystals and from the presence of small imperfections which generally reduce the resolving power to less than the theoretical. Recent development in the growing of artificial alkali halide crystals (see page 51) has led to their production

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[1] G. B. B. M. Sutherland, *Infrared and Raman Spectra*, p. 7. London: Methuen and Co., 1935.

commercially in sizes up to 125 mm high and 190 mm in diameter.[2]
These crystals are of a high degree of perfection, and 60° prisms have
been made of sodium chloride and potassium bromide with a 12 × 15-cm
face and with approximately the theoretical resolving power. With
such prisms, it is possible to construct prism spectrographs of good
resolving power and of high light-gathering power. A spectrograph
designed by E. D. McAllister is shown in Fig. 99.[3] The general design
is due to Wadsworth.[4] The light passing the entrance slit is collimated
by the parabolic mirror and, after traversing the prism, is reflected from
the plane mirror at normal incidence (for the ray at minimum deviation),
goes through the prism a second time, and is focused by the concave
mirror upon the vacuum thermopile. Accordingly, the ray which reaches
the thermopile is one which has traversed the system symmetrically
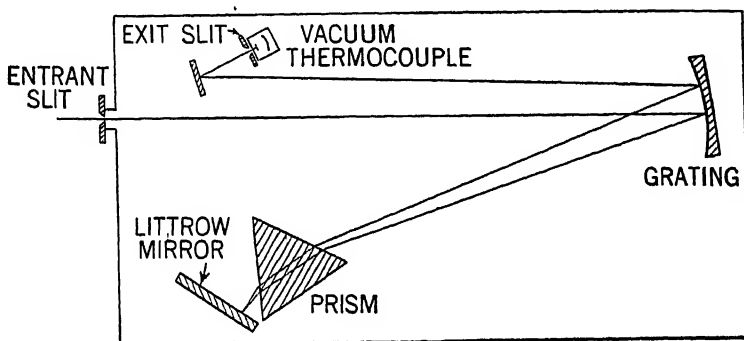
Fig. 99. Infrared Spectrograph of the Littrow Type with Rock Salt Prism.

that is, at minimum deviation. Other wave lengths are brought on the
thermopile by rotating the prism and plane mirror as a unit about the
axis. With this instrument, McAllister has reported achieving a resolv-
ing power equal to the theoretical limit of the prism (a 15-cm base twice
traversed) for all wave lengths greater than 2.5μ (the smallest wave
number intervals resolved were 6 cm⁻¹, 1 cm⁻¹, and 3 cm⁻¹ at 2.7, 6,
and 14μ, respectively).

105. Grating Spectrometers

Where higher dispersion and resolution are required in the infrared,
as for the examination of the fine structure of bands, or for the accurate
measurement of wave lengths, gratings are used. In the simplest form
of instrument, the grating would merely replace the prism in Fig. 99.

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[2] Harshaw Chemical Co., Cleveland, Ohio.
[3] E. D. McAllister, G. L. Matheson, and W. J. Sweeny, *Rev. Sci. Instr.*, **12**, 314, 1941.
[4] F. L. O. Wadsworth, *Phil. Mag.*, (5) **38**, 137, 1894.

With the higher resolving power attainable with gratings, however, there may be found to be an objectionable amount of astigmatism due to the fact that the concave mirrors must be used off-axis by either the incident or reflected beam, or both. The trouble can be partly avoided by using non-central sections of parabolic mirrors, or by having successive mirror reflections on opposite sides of the axis (see page 82). A more satisfactory method, especially for large-aperture lenses, is Pfund's method (see page 83) of using an auxiliary plane mirror.

An example of a grating spectrograph using this mirror system is the one set up at the University of Michigan by J. D. Hardy, and shown in Fig. 100.[5] The radiation passing through the entrance slit S_2 and a slot in the plane mirror P_2 is collimated by the parabolic mirror M_2 and returns on the axis of this mirror to the plane mirror P_2 and thence to
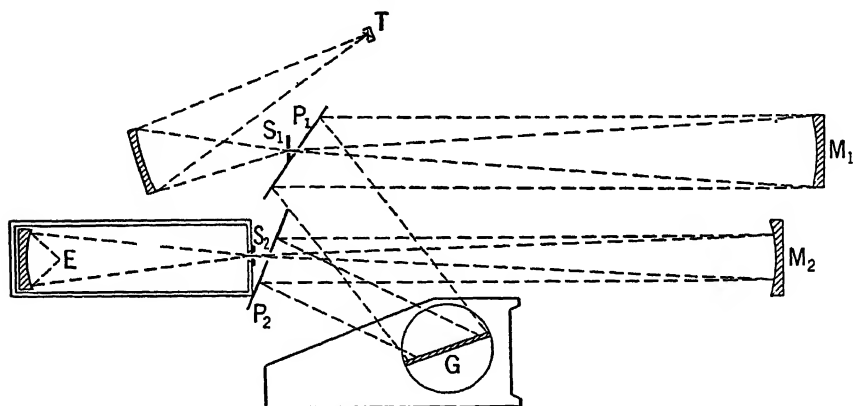
Fig. 100.   Large Infrared Grating Spectrograph with Pfund Mirror Arrangement.

the grating. After diffraction by the grating, the light follows an inverse path, to the plane mirror P_1; thence to the parabolic mirror M_1, which brings it to a focus at the exit slit S_1 after passing through the slot in P_1. Finally, an elliptical mirror with one focus at S_1 and one at T, focuses the light on the thermocouple T. For the center of the slit, at least, there is no astigmatism in this system and relatively little at the slit ends. The system involves five mirror reflections, which, however, because of the high reflecting power of the metallic mirrors used in the infrared, do not result in excessive energy losses.

In this instrument the mirror M_2 has a focal length of one meter, while at M_1 a mirror of one-meter focal length and, for large dispersion, one of four-meter focal length can be used interchangeably. The grating used in the near infrared is a five-inch plane grating with 15,000 lines to the inch. With the mirror of longer focal length, a resolving power in the near infrared of approximately 1,000 is attained. This resolving

[5] J. D. Hardy, *Phys. Rev.*, **38**, 2162, 1931.

power is, of course, far from the theoretical resolving power of the grating of 75,000. Although more recent work has resulted in somewhat improved infrared resolution, the theoretical resolving powers of the gratings used are generally not reached.[6] The limit is usually set, not by the size of the grating or by the excellence of the optics, but by the slit width required for adequate illumination. The present limit of resolution permits the separation of lines from 0.25 cm^{-1} to 0.3 cm^{-1} apart in the region from 1.5μ to 7μ, and of lines from 0.4 cm^{-1} to 0.5 cm^{-1} apart throughout the infrared and far infrared.

106. Elimination of Higher-Order Spectra

One difficulty of the grating is that higher orders of short wave lengths fall on the long, lower-order wave lengths of the same values of $n\lambda$. This characteristic is troublesome in the infrared because such shorter wave lengths are always not only present but also prominent, since the light sources used usually are much richer in near infrared and visible radiations than in infrared. Filters for this region are not very satisfactory. A common expedient in the near infrared is that introduced by Randall, who placed a prism spectrometer of small dispersion before the grating spectrograph. The prism disperses the radiation, and a small region of its spectrum is then allowed to fall on the entrance slit of the grating spectrometer.

Such prism-grating combination arrangements can be used only in the near infrared, to about 25μ, which is the limit of transparency of optical prism materials. For the long wave-length region, the spectra must be purified by absorbing screens and filters or by reflection methods, or, in emission spectroscopy, by the use of selection radiators as energy sources.

No very satisfactory selection of filters for the middle and far infrared is available. Most optical materials become opaque at points from 3μ to 40μ and are transparent to shorter wave lengths, so that, while useful for excluding long wave-length radiations, they are not useful as band-pass filters or as a means of eliminating the shorter wave lengths in an infrared spectrum. Some substances are known which, although opaque in the visible and near infrared, become relatively transparent again to longer wave lengths.[7] Paraffin, quartz, black paper, and thin antimony-black films are all quite transparent in thin layers to wave lengths longer than 50μ, and remain so to beyond 200μ. Accordingly, these materials are available for filters and also for the windows necessary before the slits and for the radiation receivers in infrared spectrometers.

[6] H. M. Randall, *J. Appl. Phys.*, **10**, 769, 1939.

[7] H. S. Seifert and H. M. Randall, *Rev. Sci. Inst.*, **11**, 365, 1940; R. B. Barnes, *Phys. Rev.*, **39**, 562, 1932.

107. Christiansen Filters

The Christiansen filter principle has also been applied in the infrared. In these filters, a transparent powder is placed in a fluid contained in a parallel-sided cell. For any wave lengths for which the powder and fluid have the same refractive index, the cell acts in the same way as a plane-parallel plate. For other wave lengths for which the two substances have different indices, a beam of light passing through the cell will be scattered in all directions, with an effect which becomes greater as the difference of the indices increases. In the infrared, advantage is taken of the fact that the alkali halides have regions of anomalous dispersion in which the index of refraction passes through unity. For this reason air is used as the fluid, and the cell, filled loosely with powdered salt, acts as a filter transmitting perhaps 50 per cent of the light in the region of anomalous dispersion, becoming opaque more or less rapidly on either side.[8] The regions of transmission of air-salt filters of this type are given in Table I.

TABLE I
CHRISTIANSEN FILTER PEAKS FOR VARIOUS CRYSTALS

Crystal	Christiansen Peak	Reststrahlen Peak
LiF	11.2μ	26μ
NaCl	32	52.0
NaBr	37	
NaI	49	
KCl	37	63.4
KBr	52	81.5
KI	64	94
RbCl	45	73.8
RbBr	65	
RbI	73	
CsCl	50	
CsBr	60	
TlCl	45	91.9
TlBr	64	117
TlI	90	151.8

Table I also shows the peaks of the rather wide bands of selective reflection, or *reststrahlen*, of some of the crystals. Two or more reflections from suitably chosen crystals, before the beam enters the spectrometer, instead of, or in addition to, the mirror reflections, result in relatively pure *reststrahlen* radiation in any region between 20μ and 150μ.

Further elimination of the effect of short-wave radiation can be attained by the use of shutters transparent to the short wave lengths.

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[8] R. B. Barnes and L. G. Bonner, *Phys. Rev.*, **49**, 732, 1941.

Thus, a glass shutter permits about 80 per cent of the radiation shorter than 5μ to pass, but excludes longer wave lengths. Any trouble from short-wave radiation can arise, then, only from the additional 20 per cent which is admitted when the shutter is opened for readings.

The infrared receiver-thermopile, or radiometer, should have as small a heat capacity as possible, in order to keep down re-radiation and to allow rapid readings of radiant energies. A suitable covering material for the junctions is of prime importance, and since different materials vary widely with wave length in their absorbing and reflecting properties, the ideal receiver surface in all these respects does not exist. The covering should, if possible, absorb the desired radiation uniformly throughout the wave-length region under examination and reject other wave lengths. Bismuth black is often used in the near infrared, and graphite (Aquadag) or powdered glass in the far infrared.[9]

108. Spectrometer Adjustment and Calibration

The adjustment of infrared spectrometers is, in general, straight-forward. Since the use of mirrors avoids the necessity of refocusing for different wave-length regions, the adjustments can be made with visible light. In the case of grating instruments, the grating is usually replaced by a good plane mirror, and a low-power microscope is focused upon the exit slit. The spectrometer mirrors can be adjusted and focused individually, in turn, until the best image is obtained at the exit slit. The plane mirror can then be replaced by the grating. No further adjustment should be necessary unless slight ruling errors of the grating cause a minor focal change or a displacement of the spectrum (see page 174).

In all infared spectrometers, the desired spectral line or region is made to fall on the exit slit by rotating the dispersing grating or prism system. The grating or prism table is usually mounted on a high-precision conical bearing and some means is provided for calibrating its position in terms of wave length. In the case of commercially built, small prism instruments, the calibration sometimes takes the form of a wave-length scale engraved on a helical drum which is mounted on the screw that turns the prism table (see page 84). In the larger instruments, the grating or prism table is provided with a graduated circle and reading microscope, by means of which the position can be read with an accuracy of about one second of arc.

Calibration is carried out by making settings on lines of known wave length. For this purpose, the mercury lines emitted by a quartz-mercury arc are often used—both the strong infrared lines at 1.014μ and above, and the higher orders of the strong visible lines. The strong

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[9] M. Czerny and H. Röder, *Ergeb. d. Exakten Naturwiss.*, **17**, 70, 1938.

helium lines in the infrared, especially the one at 1.083μ, have also been used.   Since the dispersion of the grating in the minimum-deviation position ($\alpha = \beta$) used in the infrared (see page 131) is determined by one constant, only one known line and its angular position are required for a calibration.   Further measurements in higher orders or on other lines are, of course, desirable as checks on the calibration.   For the calibration of a prism, it is necessary to determine the angular positions of numerous lines of known wave length throughout the region under investigation, and to draw a calibration curve of angle against wave length.   Sharp absorption lines of simple band spectra, whose wave lengths have been accurately measured on grating spectrometers, are often used for prism calibration.   Bands which have been used for this purpose are those of water from 5.0 to 7.9μ, of ammonia from 7.9 to 14.0μ, and of carbon dioxide from 13.8 to 15.4μ.

109. Infrared Recorders

Until a few years ago, all infrared observations were made manually by the direct setting and reading of the angular position of the spectrometer circle, together with eye observation by telescope and scale, or other reading device of the indicating instrument.   Such observations are very tedious.   Under proper conditions, however, they can be made very rapidly.   Barnes[10] has reported making readings on over 500 different settings on a grating instrument within an hour.

There has been an increasing tendency in recent years to replace direct observation by various types of recording devices which give a photographic or inked-chart graphical record of the spectrum.   Most of these devices reduce the actual time of observation; they give a continuous, rather than a point-by-point, record and, in general, yield results of as good accuracy as direct observation does, while at the same time, of course, freeing the operator from the labor of observation and of plotting data.

The recording devices are often similar to those used on recording microphotometers.   The Leeds and Northrup Speedomax recorder, with an amplifier (see page 255), has been used by McAllister with his prism spectrograph.   The Hardy recording spectrophotometer has also been used in the near infrared.   Direct photographic recording on sensitive paper has been made by means of a drum camera of the type used with the Moll recording microphotometer.

All galvanometers, when used with thermocouple detectors, suffer from zero drifts caused by slow, continuous changes of temperature.   These drifts may not be too troublesome with prism spectrometers, where the relatively abundant energy makes rapid recording possible, but with

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[10] R. B. Barnes, *Phys. Rev.*, **36**, 296, 1930.

the narrow slits and smaller energy available in grating spectra, a large amount of amplification must be used in recording instruments, and drifts may then be very troublesome, as may also the amplification of small mechanical vibrations and of Brownian movements of the galvanometer. Accordingly, special arrangements must be provided to obtain satisfactory records.

The first successful recorder for infrared grating spectra was developed by Firestone.[11] This device takes advantage of the principle of the Pfund resonance radiometer, which interrupts the radiation to be measured at intervals which coincide with the period of the two slightly damped galvanometers that are used in the amplifying and indicating systems, respectively. These two galvanometers are more sensitive to
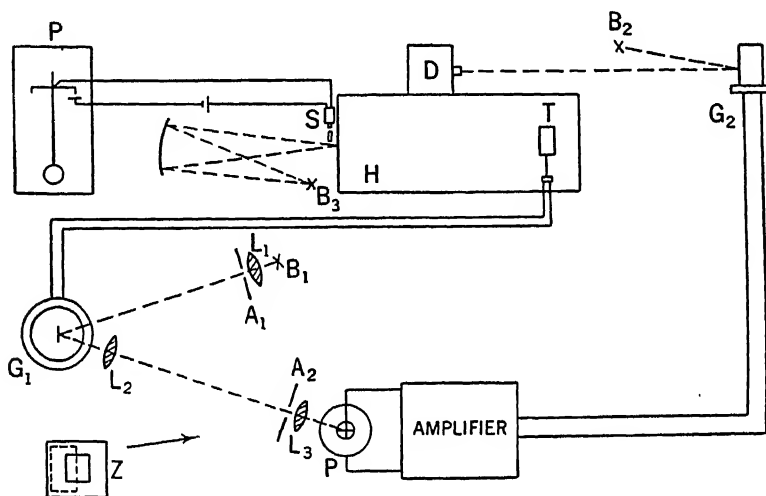
Fig. 101.   Firestone Resonance Recorder for Infrared Spectrograph.

signals of the periodicity to which they are tuned than to the irregular Brownian or mechanical motion or the slow drifts. This Pfund system is very slow in response, however, because of its sharp tuning, so that from 100 to 150 seconds may be required for a single observation.

It was found by Firestone that, if the galvanometers were of short period and approximately critically damped, the drifts could be entirely removed by the amplifying system connecting the two galvanometers while a time of response of the order of six seconds could be achieved, although the suppression of Brownian movement was not so effective as in the Pfund system. The arrangement is shown in Fig. 101. The electromagnetically driven pendulum P actuates the electromagnetic shutter S, which periodically interrupts the radiation from the source B_3

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[11] F. A. Firestone, *Rev. Sci. Inst.*, **3**, 163, 1932.

as it enters the slit of the recording spectrometer H. After passing through the spectrometer, the radiation of a selected wave length is focused on the thermocouple T, which is connected to the primary galvanometer G_1—a high-sensitivity, low-resistance instrument of 3.6-second period, which is critically damped. Light from the headlight bulb B_1 passes through the one-inch-square aperture A_1 and is focused by the lens L_1 on the galvanometer mirror. The lens L_2 forms on the $\frac{5}{8}$-inch-square aperture A_2 a displaced image of the aperture A_1, as shown at Z, and the lens L_3 forms on the sensitive surface of the photocell P an image of the filament image at the mirror. Thus, the image on the photocell varies in brightness, since, as the galvanometer mirror turns, the amount of light passing through the aperture A_2 is varied linearly by the displacement of the image of A_1.
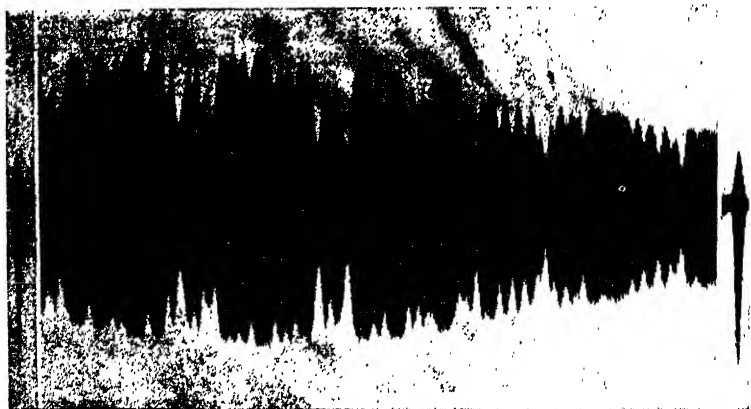
Courtesy of Professor H. M. Randall.

Fig. 102.   Record of Absorption Spectrum of Deuterium Oxide between 34μ and 38μ.

The photocell, then, delivers to the amplifier a current which varies in intensity with the deflection of the galvanometer G_1 and which is interrupted with a periodicity of 1/3.6 cycles per second. The single-stage amplifier uses a single electrometer tube, FP-54. Two large condensers, of 1.0 and 10. microfarads, respectively, are placed one on either side of the tube, and, while not seriously reducing the 1/3.6-cycle current, they effectively prevent the passage of direct current, or of drift current. The amplified current is delivered to the second critically damped galvanometer G_2. A light beam from this galvanometer traces a record on the recording drum, D, which is driven by the same motor that rotates the dispersing prism or grating to bring successive wave lengths on the thermocouple.

The photographic record thus obtained of the oscillations of the recording galvanometer is a band whose width varies with the intensity of the radiation falling on the thermocouple. Fig. 102 shows such a

record of the rotational spectrum of deuterium oxide between 34μ and 38μ made by N. Fuson at the University of Michigan.[12]　The envelope of the figure is, of course, the graph of the absorption of the molecule as a function of angular position of the grating.

It will be noted that there is no apparent drift, although it required about eight hours to produce the record.　Brownian movement, however, is apparent in the slight irregularities in the envelope and, in fact, sets a limit to the amplification which can be usefully employed.　Experience with these records has shown that measurements of line positions can be made with at least as good accuracy as is attained with the best manual operation, and that faint lines which are overlooked or omitted as uncertain in manual observation are regularly measured.　The labor of reducing results is no greater than that of plotting manual records, and can, furthermore, often be completed on one record while another is being made.　It is to be expected that, in the future, automatic recording of infrared spectra will be as much a routine procedure as is photographic recording of shorter wave-length spectra at present.

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[12] N. Fuson, H. M. Randall, and D. M. Dennison, *Phys. Rev.*, **56**, 982, 1939.

CHAPTER 12

The Spectroscopy of the Vacuum Ultraviolet

The vacuum ultraviolet region of the spectrum is the short wave length range, beginning at approximately 1850A, to which air, even in thin layers, is opaque. Observations must, consequently, be made with the whole light path in a good vacuum. The experimental methods in this region are determined not only by this limitation but by the further limitations that few optical substances are transparent at all in the extreme ultraviolet and none to very short wave lengths, and that the ordinary photographic plate fails at wave lengths shorter than about 1850A because of the increasing opacity of its gelatin.

110. The Work of Victor Schumann

These three fundamental properties of the extreme ultraviolet were all discovered by Victor Schumann, who, as was noted in Chapter 1, devoted his leisure time for twenty years to pioneer work in the region. The oxygen of the air, the gelatin of the photographic plate, and the quartz optics commonly used in ultraviolet spectrographs, all become opaque at nearly the same point, that is, near 1850A. The determination and removal, one by one, of these limitations to extreme ultraviolet spectroscopy was Schumann's great contribution. He removed the oxygen by evacuating the whole optical system; he replaced the quartz optics by fluorite, which he had determined to be more transparent; and, finally, he developed the practically gelatin-free photographic plates which still bear his name. These procedures enabled him to extend the spectrum to the vicinity of 1200A, although he had no means of determining wave lengths in this new domain.[1]

In general, fluorite vacuum spectrographs have all the optical characteristics of the prism spectrographs used in longer wave length regions. Schumann's spectrograph, and those of most of his successors, was of the Babinet Bunsen, or straight-through, type, with a narrow slit and with collimator and camera lenses and prism of clear fluorite; R. Frerichs, however, designed a fluorite vacuum spectrograph of the Littrow type,

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[1] The work of Schumann is fully discussed by Theodore Lyman in *Spectroscopy of the Extreme Ultraviolet*, 2nd ed., New York: Longmans, Green and Co., 1928. Lyman gives a complete bibliography of Schumann's papers.

using a Hochheim-alloy reflecting coating on the back of a 30° fluorite prism.[2]

The relative inefficiency of vacuum pumps in his day led Schumann to keep the volume to be evacuated as small as possible and to provide for making all the adjustments from outside without disturbing the vacuum. Modern rapid vacuum pumps render such arrangements less important, and recent fluorite spectrographs have been simpler and somewhat bulkier in design, with few, if any, external adjustments. Examples are the spectrograph of McLennan and Lewis,[3] in which the prism and camera are placed in a bronze cylinder, 30 cm in diameter, with a ground-metal coverplate, while the collimator is in a side tube; and the small instrument of Cario and Schmidt-Ott,[4] in which the optical system is mounted on a base plate and slipped as a whole into a cylinder only 30 cm long and 7 cm in diameter. This little instrument has lenses of 8-mm diameter and 100-mm focal length, and a 60° prism 7 mm high. Its dispersion at 1400A is about 6A per millimeter; it is rapid and adequate for much survey work, for work in photochemistry, and for absorption or fluorescence spectroscopy.

As in the case of all prism spectrographs, wave-length determinations can be made with the fluorite vacuum spectrograph only after calibration of the spectra with lines of known wave length. Therefore, calibration of the spectra of Schumann and his immediate successors had to wait the development of ultraviolet standards. Such standards were first established by Theodore Lyman in 1906, when, as noted in Chapter 1, he applied the concave grating to the vacuum spectrograph.

111. Lyman and the Vacuum Grating Spectrograph

In grating spectra, as has been pointed out previously, wave lengths can be calculated from a knowledge of the grating constant and the angles of incidence and diffraction. In fact, it was by this method that the first absolute wave-length determinations were made. This method is limited by the difficulty of determining the angles precisely, which Lyman avoided by his double-slit device (Fig. 103). The spectra produced by the slits (S and S') will be displaced with respect to one another by approximately the same distance as the slit separation, and this displacement, expressed in wave length, will be approximately constant if the interval is so small that dispersion is nearly constant throughout the region.

The arrangement is calibrated by photographing known spectra through the two slits and observing the wave-length difference between

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[2] H. Bomke, *Vakuum-spektroskopie*, p. 37. Leipzig: Barth, 1937.
[3] J. C. McLennan and A. C. Lewis, *Proc. Roy. Soc.*, **98**, 109, 1920.
[4] G. Cario and H. D. Schmidt-Ott. *Zeits. f. Physik*, **69**, 719, 1931.

the two spectra. In Lyman's work, this displacement was 1180A. Accordingly, if a vacuum-region spectrum is photographed through one slit and a known longer wave-length spectrum through the other, ultra-

Fig. 103. Diagram of the Lyman Double-Slit Device for Determining Vacuum-Spectrograph Wave Lengths.

violet wave lengths are readily determined by subtracting 1180A from the lines of the second-slit spectrum with which they coincide.

Lyman rephotographed and identified Schumann's spectra, and found them to extend to the strong hydrogen line at 1215A. Lyman's own ultraviolet spectra of gases and metallic sparks extended to 500A. His mounting was of the form now known as the Eagle type, with a grating of 50-cm radius of curvature enclosing a brass tube of 91-mm internal diameter. His spectrograph is described fully in his *Spectroscopy of the Extreme Ultraviolet* and in Baly's *Spectroscopy*.

Lyman's instrument is the prototype of all later normal-incidence vacuum spectrographs, although some later ones have been somewhat more convenient to adjust and to use. Some instruments have been built to permit adjustment of the grating from the outside through
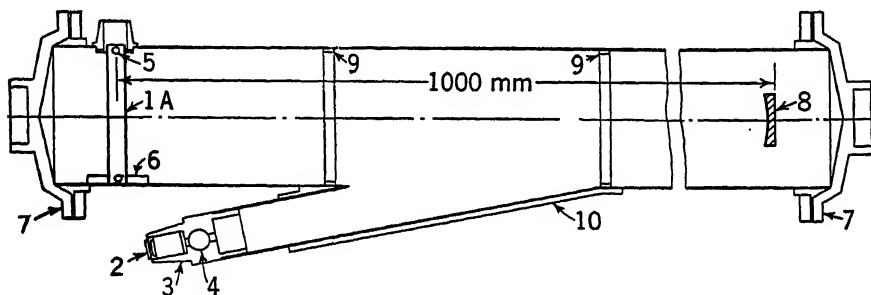
Fig. 104. Vacuum Spectrograph Design of Sawyer. *2*, slit; *4*, stopcock; *5*, plate-holder pivot; *8*, grating.

vacuum-tight motions.[5] Another form of mounting designed by H. G. Beutler has been described in Section 62. A type in which all adjustments can be made before sealing the instrument is manufactured by Adam Hilger, Ltd., of London, along the lines of the design given by Sawyer.[6]

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[5] An example is the spectrograph of W. Tschulanowsky, *Zeits. f. Physik*, **82**, 134, 1933.

[6] R. A. Sawyer, *J. Opt. Soc. Am.* and *Rev. Sci. Instr.*, **15**, 303, 1927.

The essential features of the design are shown in Figure 104. The slit *2* is mounted in the end of a side tube which is attached to the 6-inch-diameter main tube. The 1-meter grating, in a mounting giving a focusing motion as well as permitting rotation about three mutually perpendicular axes, is at one end of this tube; the tubular plate holder is inserted through a side opening. A stopcock at *4* permits closing the spectrograph to light and air from the slit while light sources are being changed or conditioned. A ground cone *3* on the end of the slit arm makes source mounting and changing easy. Both ends of the spectrograph, as well as the plate-holder opening, are closed by conical ground joints. The 15,000-lines-per-inch grating has a dispersion of about 17 A/mm, so that about 3000A are photographed on the plate in one exposure.

Adjustment of the spectrograph is made very simply in air. The plate holder slides in a tube pivoted at *5*. With any convenient light source, such as an incandescent bulb before the slit, the direct image of the slit is brought to this axis and, with an eyepiece, is focused visually from behind by the adjustment of the grating in its holder. The only remaining adjustment is the rotation of the plate holder about *5* until the long wave length end of the plate is brought into focus. This adjustment is made in air with any convenient light source which gives sharp lines in the 2000–2500A region. Since the plate is bent to the curvature of the Rowland circle, the whole plate is then in focus and will remain so when the spectrograph is evacuated.

The location of the slit on a side arm leads to a larger angle of incidence than is the case when the slit is in the spectrograph tube proper. With instruments of medium dispersion, however, the coma is not troublesome, while the astigmatism is less than for smaller angles of incidence (see Sec. 50). Important advantages of this slit location are the greater ease of attaching light sources and of placing diaphragms to eliminate stray and reflected light.

A two-meter spectrograph employing these focusing adjustments and a slit on a side arm has been designed by Compton and Boyce.[7] The spectrograph case is not a tube, but a flat, sector-shaped box made of heavy plates, thus providing space for a photographic plate 50 cm long. Among larger vacuum spectrographs may be mentioned those at the Massachusetts Institute of Technology and at the University of Wisconsin, which have six-meter concave gratings.

112. The Grating at Grazing Incidence

The wave-length range attainable by normal-incidence vacuum spectrographs, extended by Lyman to 500A, was further extended to about 200A by Millikan and Sawyer[8] through the application of the

[7] K. T. Compton and J. C. Boyce, *Phys. Rev.*, 40, 1038, 1932.
[8] R. A. Millikan and R. A. Sawyer, *Science*, 50, 138, 1919.

vacuum spark, which has higher excitation and operates in a higher vacuum than were possible with earlier sources.   Shorter wave lengths than are reached with near-normal incidence were first photographed with the use of high angles of incidence by Hoag in 1927.[9]   This development followed the demonstration four years earlier by A. H. Compton[10] that X-rays striking nearly tangentially on a metal surface undergo total reflection.   Total reflection is used with great success in the region below 1000A, where the reflecting power of all known substances is very poor.   A diagram of the concave grating mounting with high angle of incidence is shown in Fig. 105.   Seigbahn and his associates, Ericson, Ekefors, and Edlén, have been active in the design and use of vacuum
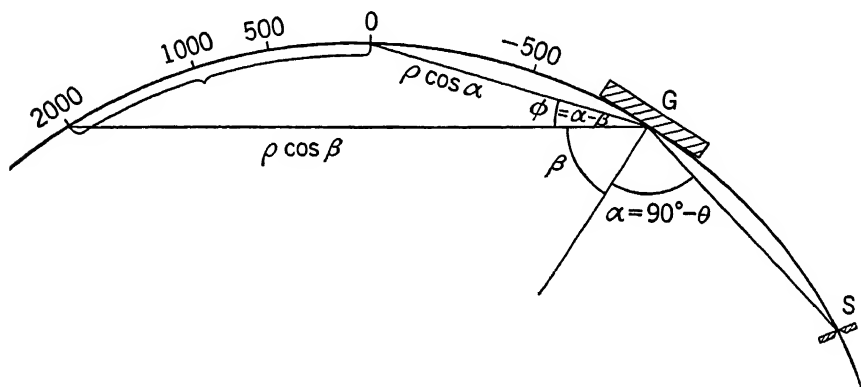
Fig. 105.   Diagram of Vacuum-Grating Spectrograph with Large Angle of Incidence. S, slit; G, grating.   The spectrum is photographed in the range 0 to 2000A.

grating spectrographs with high angles of incidence, and have described the construction of several instruments.[11]

Various angles of incidence have been used in this type of spectrograph, and some instruments have provided for several different angles. The choice of angle depends on the wave-length range to be investigated, since, from the formula for critical angle,

$$\sin \theta_c = \frac{e}{c} \lambda \sqrt{\frac{N}{\pi m}}$$

where e and m are the charge and mass of the electron, c the velocity of light, N the number of electrons per unit volume, $\theta = 90° - \alpha$, and λ the wave length above which there is critical reflection.   Sin θ is proportional to λ, and for $\theta = 10°$, all wave lengths above 40A are totally reflected.

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[9] J. B. Hoag, *Astrophys. J.*, **66**, 225, 1927.
[10] A. H. Compton, *Phil. Mag.*, **45**, 1121, 1923.
[11] B. Edlén and A. Ericson, *Zeits. f. Physik*, **59**, 656, 1930; E. Ekefors, *Zeits. f. Physik*, **71**, 53, 1931.

The actual wave-length limit that will be attained by any instrument will depend not only on the angle of incidence, but also on the light source, photographic plates, exposure, and other factors. Some observations were made on the efficiency of a grating at various angles of incidence by Edlén,[12] who gave the following results:

Angle of Incidence	Shortest Wave Length Obtained
0°	320A
60°	160A
80°	75A
85.6°	53A

With another instrument, using an angle of incidence of 89°, Tyrén observed wave lengths as short as 12.1A.[13]

With increase in the angle of incidence, the astigmatism of the grating increases rapidly, while the usable width of the grating decreases.[14] The increased reflecting power to some extent compensates for these effects, and the exposures are not much longer than for normal-incidence spectrographs.

As can be seen from Equation (61), page 137, and Figure 55, the dispersion of high-incidence spectrographs is much larger than that of the normal-incidence types, and varies much more rapidly with wave length. For example, a 1-meter grating with 14,500 lines per inch at 80° incidence has a dispersion at 1000A of 6.5A/mm, and at 100A of 2.5A/mm, in contrast to its dispersion at normal incidence of about 17A/mm.

The adjustment of grazing-incidence spectrographs is somewhat more difficult than the adjustment of near-normal-incidence spectrographs. The large astigmatism makes necessary very accurate leveling of the grating and adjustment of its rulings to make them parallel with the slit. The large angles of incidence and diffraction call for accurate focusing, since small errors produce a displacement in line position which depends upon the tangent of the angle. Because of the large angles at which the rays strike the photographic plate, it is essential that the plate fit the focal curve accurately. For this reason, many observers have used thin plate glass in making Schumann plates.

Preliminary adjustments of the grating and the focusing of the direct image can be done in air, but final adjustment and focusing must, of course, be done in vacuum. Detailed plans for the complete adjustment

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[12] B. Edlén, *Nova Acta Reg. Soc. Sci. Ups.*, IV, **9**, No. 6, 1934.

[13] F. Tyrén, *Zeits. f. Physik*, **111**, 314, 1938.

[14] J. E. Mack, J. R. Stehn, and B. Edlén, *J. Opt. Soc. Am.*, **22**, 245, 1933; J. E. Mack and J. R. Stehn, *J. Opt. Soc. Am.*, **23**, 184, 1933; R. O. Anderson and J. E. Mack, *J. Opt. Soc. Am.*, **24**, 292, 1934.

of grazing-incidence spectrographs have been given by, among others, Ekefors,[15] and by Rathenau and Peerlkamp.[16]

113. Gratings and Technique for the Ultraviolet

Gratings for use in the ultraviolet were originally ruled on speculum metal and were, in fact, identical with those used at longer wave lengths. It was found, however, that such gratings were relatively ineffective below 500A. Millikan and his associates observed that lightly ruled gratings, with reflecting areas left between the grooves, were much more effective.[17] Especially for grazing-incidence spectrographs, it is advantageous to have smooth ruled surfaces. For this reason, O'Bryan[18] has recommended etched-glass gratings for this use and lightly ruled speculum or glass gratings for near-normal incidence. Glass, however, is a relatively poor reflector above the region of total reflection. Aluminum has the best reflecting power through most of the vacuum region. It is most conveniently used as an evaporated layer on a glass or speculum grating. When the surface becomes tarnished, the aluminum is easily removed by sodium hydroxide and a new coating applied.

The technique of vacuum spectroscopy, although somewhat more troublesome than that of ordinary spectroscopy, is no longer very difficult. Modern high-speed oil or mercury-vapor pumps can readily evacuate even 21-ft. concave-grating spectrographs. The technique of making Schumann plates has been described by several workers since the early discussions of Schumann and Lyman.[19] Hilger in England and Agfa in Germany have produced good Schumann plates commercially. Ilford Q plates and Eastman Ultraviolet-sensitive plates are somewhat more convenient to use than Schumann plates and are sensitive to wave lengths at least at short as 100A, although, up to the present, the contrast and resolving power of these plates are not quite so good as in Schumann plates.

Wave-length calculations with the normal-incidence type of instrument can be made and, at first, were necessarily made by use of the grating formula, with suitable corrections for nonlinearity of dispersion.[20] However, all wave-length determination is now made with the aid of standard wave lengths, either superimposed on or included among the lines to be measured.

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[15] E. Ekefors, *Zeits. f. Physik*, **71**, 53, 1931.

[16] G. Rathenau and P. E. Peerlkamp, *Physica*, **2**, 125, 1935.

[17] R. A. Millikan and R. A. Sawyer, *Phys. Rev.*, **12**, 168, 1918; R. A. Millikan and I. S. Bowen, *Phys. Rev.*, **23**, 1, 1924.

[18] H. M. O'Bryan, *Phys. Rev.*, **38**, 32, 1931.

[19] For example, J. J. Hopfield and E. T. S. Appleyard, *J. Opt. Soc. Am.*, **22**, 488, 1932.

[20] R. A. Millikan, I. S. Bowen, and R. A. Sawyer, *Astrophys. J.*, **53**, 150, 1921.

114. Ultraviolet Light Sources

The requirements for a light source in the ultraviolet are: first, that it be capable of operating in high vacuum, or at least at very low pressures; and second, that its excitation be adequate to produce the high-frequency radiation desired. For wave lengths below about 500A, little radiation is emitted by any but spark discharges. The very shortest wave lengths are emitted only by the vacuum spark, first used by Millikan and Sawyer in this region.[21] This source was used by Edlén, with a 0.4-microfarad condenser charged to 50,000 volts, to produce the highest spectral excitation yet recognized, Cu XIX.[22]

Where the excitation of atoms only two or three times ionized is to be studied, other sources can be used and may be preferred because of selective or limited excitation, excitation of high-series members, or for other reasons. Such sources include: (a) arcs or sparks in gases, such as nitrogen, hydrogen, or the noble gases, which are transparent throughout all or most of the region; (b) electrodeless discharges in gases or metallic vapors; (c) the hollow-cathode discharge of Paschen.

For absorption measurements in the region, a continuum can be obtained down to 1600A from a high-current discharge in hydrogen, while a similar discharge in helium gives a continuum from 900A to 600A. A condensed discharge through a capillary, first used by Lyman, produces an uninterrupted continuum from the visible down to at least 270A.[23] Fuller discussions of suitable sources for use in the vacuum region will be found in the monographs of Boyce and of Bomke.

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[21] R. A. Millikan and R. A. Sawyer, *Science*, **50**, 138, 1919.

[22] B. Edlén, *Zeits. f. Physik*, **100**, 621, 1936.

[23] G. Collins and W. C. Price, *Rev. Sci. Inst.*, **5**, 423, 1934.

CHAPTER 13
Spectrochemical Analysis

To an ever-increasing extent the spectrograph is being used to determine the composition of a wide variety of materials and to fix the concentration of their constituents. Known to the chemist as qualitative and quantitative analysis, respectively, these spectroscopic techniques are commonly referred to as spectrochemistry or as spectrochemical analysis, usually without the adjectives *qualitative* and *quantitative*.

The development of spectrochemical analysis is, of course, an outgrowth of the recognition, about the middle of the last century, that the spectrum emitted by an atom is characteristic of that atom and of its energy condition. It has already been pointed out in Chapter 1 that Kirchhoff and Bunsen were the first to recognize this principle clearly and to use it in the isolation and discovery of two new alkali elements, caesium and rubidium.

115. Qualitative Spectrochemical Analysis

This work by Kirchhoff and Bunsen constituted the first qualitative analysis. These experimenters recognized, after a study of the spectra of the known alkali elements, that certain spectral lines not belonging to the pure spectra of the known alkalies appeared in the light emitted by some of their preparations. Their search for the origin of these lines led them finally to the isolation of the new elements. At the same time, they were applying their knowledge to the study of the Fraunhofer lines and to the identification of numerous elements in the sun's atmosphere. Qualitative spectrochemistry was firmly established by these achievements. It has, of course, been extended in scope, precision, and sensitivity by later work.

Today, under proper conditions, the spectrograph provides the most rapid and, at the same time, the most sensitive technique for qualitative analysis. In Section 92, the procedures have been discussed for determining from the spectrum what elements are present in a source or for deciding whether or not any atom or molecule is present in detectable amounts. The attributes of various light sources which are suitable for spectrochemical investigations have been discussed in Chapter 2. The application of these and other necessary techniques to spectrochemistry will be discussed in this chapter.

When the problem is the detection and analysis of atoms rather than of molecules, the emission spectrum will commonly be employed, and the light source and spectrograph used will be those that are adapted to the nature and available quantity of the sample. Solid conducting samples are generally most conveniently used in a d-c or a-c arc. In this case, the samples may be of almost any size or shape and may be mounted in any electrode holder. For materials with low melting or ignition points, water- or air-cooled electrode holders may be desirable, and it will be necessary to hold the current strength at levels that will not lead to overheating of the electrodes.

Poorly conducting or refractory materials, or materials available in minute amounts only, may be packed in cavities drilled in a graphite, silver, or copper electrode. If the material is nonconducting, or if it does not pack well, it may be mixed with powdered graphite. Solutions can be handled in the arc by drying a drop or so of the concentrated solution on the tips of graphite electrodes. In all these cases, the upper electrode is usually of the same material as the lower. When any foreign electrode—graphite or other—is used, it is necessary to run blank exposures with the uncharged electrodes to determine the impurities, if any, in the electrode materials, as well as the lines emitted by the electrodes themselves. In this connection, it must be borne in mind that, when the sample material is placed in or on the electrodes, the changed electrical gradients and temperatures in the arc may bring out lines from the electrodes which were seen only faintly, if at all, in the blank tests.

Solutions may also be examined by atomizing them into a flame, as has been done by Lundegårdh,[1] or by sparking between two liquid electrodes, as, for example, by the method of Duffendack, Wiley, and Owens.[2] For qualitative purposes, at least, these procedures seem not to be so convenient or so rapid as that of drying the solution on a graphite electrode.

The spark may be used, also, between solid electrodes for qualitative analysis, but the much smaller resultant sensitivity to trace concentrations tends to discourage the use of spark techniques.

By emission methods, analysis may be made for all of the metallic elements and, with less sensitivity in general, for the metalloid and a few nonmetallic elements. The list of detectable elements includes at least 55 in addition to the rare earth elements, the spectra of which are rapidly becoming well enough known to be readily recognized. Practically every element can be observed by the ordinary methods of emission spectroscopy, except that the gaseous elements can ordinarily be detected only in discharge tubes, and the sensitive lines of sulphur lie in the vacuum ultraviolet region.

[1] H. Lundegårdh, *Zeits. f. Physik*, **66**, 109, 1930.
[2] O. S. Duffendack, F. H. Wiley, and J. S. Owens, *Ind. Eng. Chem.*, **7**, 410, 1935.

It is not necessary for the elements to be present in uncombined form. The temperature of any of the ordinary sources is sufficient to dissociate any molecules and to excite the resulting atoms.   In fact, it is one of the weaknesses of emission spectrochemistry that it gives little information on the state of combination of atoms in the source material, although it is often an advantage that the total amount of any element is measured in quantitative spectrochemistry regardless of the various compound forms in which it may be present.

116. Trace Detection

In qualitative spectrochemistry, the major constituents of the source material are readily recognized from the "sensitive" and other prominent lines of these elements.   An extremely important question in many analysis problems, however, is the identification of trace elements which may be of importance even when present in amounts not detectable by conventional chemical methods.

It must be borne in mind that the absence of the detection lines of an element indicates merely that the element is not present in sufficient amount to be detected with the source and equipment used.   Experience with the apparatus, as well as some knowledge of the make-up of the sample under examination, is necessary before an estimate can be formed of the minimum observable amount of any element.

There are, in fact, wide variations in the relative spectral sensitivity of the different elements and of the various light sources.   Thus arcs are, in general, much more sensitive than spark sources, and the spectra of the metals much easier to excite then those of the metalloids.   The intensity with which the spectrum of an element is excited depends also, to a considerable extent, on its properties relative to those of the other elements in the sample.   In general, an element of low boiling point, high vapor pressure, or low ionization potential will be excited more strongly than elements in the same sample with higher boiling points or ionization potentials, or with relatively lower vapor pressures at the electrode temperatures.

Under favorable conditions, the presence of an element in concentrations as low as one part in a million is readily detectable.   Owens,[3] who used solutions dried on the tips of graphite electrodes, reported, in the analysis of caustic liquors, an absolute sensitivity of as little as 1×10^{-6} mg of the test element on the electrodes, and a relative sensitivity for manganese as low as 0.000002 per cent.   On the other hand, an unfavorable example is the determination of tin in minerals, by van Tongeren.[4] With a glass spectrograph, with the cathode layer of a d-c arc as the

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[3] J. S. Owens, *Ind. Eng. Chem.*, **11**, 59, 1939.

[4] W. van Tongeren, *Chemical Composition of the Earth's Crust in the East Indian Archipelago.*   Amsterdam: Centen, 1938.

source, and with the powdered sample mixed with graphite and sodium carbonate and packed in the cavity of a graphite electrode, he reported 0.3 per cent of tin in SnO_2 as the least detectable concentration. His results, however, would certainly have been greatly improved if the much more sensitive ultraviolet tin lines could have been used rather than those in the visible (glass spectrograph) region.

Many examples of the sensitivity of the determination of various elements in different sources and in the presence of other major constituents are to be found in the literature cited and in other papers in the field. Since the sensitivity of trace determination depends so much on the spectrograph, the photographic plate, the light source, and the spectral region used, as well as on the other elements present in the sample, it is best, if previous experience in comparable cases is lacking, to undertake some comparative tests on samples of known similar composition before reaching a conclusion on whether or not any element is present in appreciable amount.

In general, under suitable working conditions, the sensitivity of trace analysis of metals by line emission methods is better than that of chemical wet methods and as good as or better than colorimetric methods. The speed is usually greater, especially if suitable master charts or spectra are available for rapid identification or comparison. The specimens can ordinarily be used in their natural form: as solid electrodes; as liquids dried on the ends of graphite or silver electrodes; as powders or nonconductors packed in cavities in graphite electrodes. A few minutes is sufficient to expose and process a plate, and the examination of the spectra is rapidly made in all but the most complicated cases.

While one important use of the spectrograph is in the examination of samples for traces of impurities, a no less important use is in the rapid examination of samples of many kinds to determine what elements are present and which, if any, need to be determined quantitatively by more laborious chemical methods. Many examples of this sort of analysis will be found in the *Proceedings of the Summer Conferences on Spectroscopy and its Applications*, listed in the bibliography at the end of this chapter. In this connection may be mentioned the sorting of scrap steels as to alloy type in steel mills, which may, in fact, be done with a visual spectroscope (page 85); the classification of minerals; and the detection of metallic poisons in criminal investigations.

It can be seen from the foregoing discussion that the applications of qualitative analysis with the spectrograph are as varied as those of chemical methods. The spectrographic method has the great advantages of speed and simplicity in a technique that can handle a wide variety of samples with the same equipment and procedure.

The earliest practical applications of the spectrograph were qualitative, and these are still the commonest and best known. They can hardly

be successfully carried out, however, without some understanding of the quantitative use of the spectrograph. To an increasing extent, the two techniques are used in conjunction. Moreover, quantitative spectrochemistry is rapidly gaining in use and acceptance and bids fair, in the future, to become the more important analytical use of the spectrograph.

117. Quantitative Spectrochemical Analysis

Quantitative spectrochemical analysis is based on the fact that when an element is present in a matrix—a body of other materials—in small and decreasing amounts, its spectral lines grow gradually weaker and disappear in a definite order, while their intensities at any concentration are simple functions of the concentration. An example of this influence of
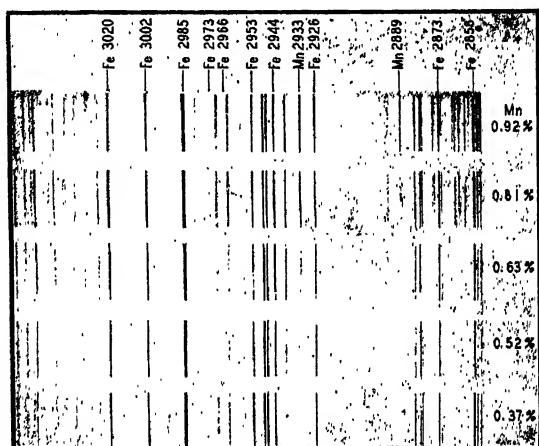
Fig. 106. Spectrograms of Samples of Iron Containing Manganese in Different Amounts.

abundance or concentration on the strength of the spectrum of a substance present in small amounts in a sample is seen in Fig. 106, which shows a series of iron spectra containing small known percentages of manganese. As nearly as possible, the spectra were made under identical conditions, as is shown by the uniform intensity of the marked iron lines. The manganese lines decrease in intensity with decreasing concentration and disappear at different percentage contents in the sequence. The first systematic study of this effect was made by Hartley, at Dublin, in 1882. His work laid the foundations of quantitative analysis by the spectrum, and he actually made the first quantitative analysis—that of beryllium in cerium compounds.

Hartley, and his immediate successors, such as Pollock, at Dublin, and de Gramont, at Paris, made their analyses by comparing visually the spectra of their samples with those of a graded series of similar and

known composition and by choosing the known spectrum which best matched that of the unknown sample. Such methods of matching spectra, especially if there is not careful selection and control of the source, can hardly be expected to give any but the roughest accuracy—perhaps 10–25 per cent at best. The intensity of the spectral lines of a minor or secondary component in a source is influenced not only by the characteristics of the spectrographic apparatus and by the photographic technique, but also by the nature and amount of other elements in the electrodes and by random fluctuations in the operation of the source.

The development of spectrochemical analysis in recent years to a point where it attains an accuracy comparable with that of chemical analysis and a speed much greater has followed from a careful study of each step of the process, which has resulted in more consistent and controllable light sources, better photographic materials, more direct comparison methods, and, above all, precise photometry of spectral line intensities.

118. The Internal-Standard Principle

Almost without exception, all precision quantitative analysis utilizing emission spectra is based on some variant of the internal-standard principle first enunciated by Gerlach.[5] As noted earlier, a major difficulty in all methods of matching spectra arises from light-source fluctuations, which can result in spectra of unequal over-all intensity and intensity distribution, from samples of identical composition. Gerlach observed that many of these difficulties of "external reference standards" are avoided when a chosen line of the element under analysis is compared with a line of some reference element in the same spectrum. Qualitatively, at least, the two lines will respond in the same way to random source fluctuations—they cannot do so exactly unless both lines have identical excitation functions and unless both elements have identical vapor tension-temperature relations.

For each of several known concentrations of the element under analysis, Gerlach's method is to choose a reference pair consisting of a line of the analysis element and a line of the reference element of equal intensity at that concentration. It is assumed that, if the two lines of a reference pair appear with equal intensity in the spectrum of any sample, the concentration of the analysis element will be the same as in the reference samples whose spectra had been previously studied. Analysis of an unknown sample can then be carried out by selecting visually the one of these reference pairs in the spectrum for which the two lines are of equal intensity. Most of the modern procedures use only one such pair

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[5] W. Gerlach, *Foundations and Methods of Chemical Analysis by the Emission Spectrum*, Chap. V. London: Hilger, 1929.

of lines.   Their relative intensities are determined by some photometric procedure and plotted as a function of concentration.   The resulting graph serves as the basis for the determination of the concentration of any unknown sample.   If the two variables are plotted on logarithmic scales, the resulting "analytical curve" over a considerable range is usually very close to a straight line.   An example from the determination of manganese in iron is given in Fig. 107.

In practically all cases it is impossible to select a reference element such that lines of the spectrum of the unknown and of the reference element can be found which respond in exactly the same way to source fluctuations.   It is therefore essential to select a pair of lines which
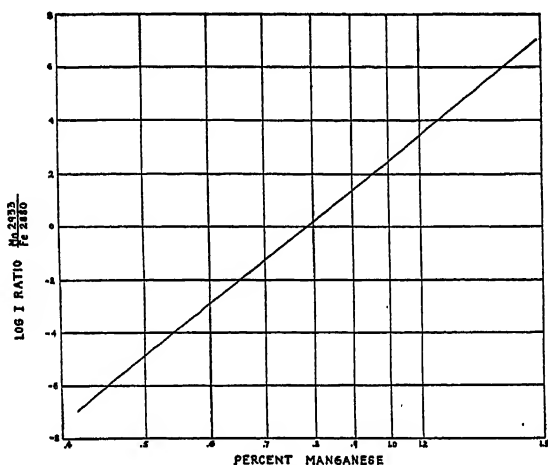
Fig. 107.   Analytical Curve.   The relationship is shown between percentage content of manganese in the sample and the relative intensities of analysis line pair.

behave as similarly as possible under varying conditions; such line-pairs were called by Gerlach *homologous pairs*.   Since proximity in wave length avoids variation in plate contrast, and proximity on the plate minimizes errors due to variation in emulsion sensitivity from point to point, a rough selection of line-pairs may be made by choosing a reference element of approximately the same ionization potential and vapor pressure as the analysis element, and then choosing from the two elements a pair of lines which, for the median concentration to be determined, have about equal intensities and are near together.   In any case, the density of the reference line should fall within the working range of density of the analysis line—in general, in the density range from 0.3 to 1.0.

In the case of liquid or powdered samples, the internal-standard material can readily be added.   From the wide range of choices, an element of proper excitation properties can often be found.   Furthermore, by the proper choice of the amount of reference material to be

added, the intensity, relative to the analysis line, of any desired reference line can be changed within a considerable range. In the case of solid samples, the problem is to find a reference line from the spectra of the matrix constituents which are present in such large amounts that their line intensities are unaffected by any likely variations in the content of the minor constituents.

Many suitable line-pairs will be found mentioned in the literature of spectrochemical analysis. The choice is influenced by the source conditions used, as well as by the percentage range of content to be covered. It is always advisable, in undertaking a new analysis problem, to test several possible alternate line-pairs. Measurements should be made on the spectra of four or more samples of known composition covering the analysis range. If the intensity ratios are plotted against concentration on logarithmic scales, as in Fig. 107, there will ordinarily be found variations for the different pairs both in the slope of the resulting analytical line and in the extent of scatter of the individual points about the line. A pair should be selected which gives a good slope and as little scatter as possible. A good slope insures good sensitivity in the determination, while little scatter indicates good repeatability or accuracy. The accuracy, however, should be checked by repeated determinations on the same sample.

119. Choice of Light Sources

The accuracy attainable is greatly influenced by the choice of light source, as are also the sensitivity and the analytical range. In fact, in the best modern practice the controlling error is that introduced by the random fluctuations of the light source. The ideal spectrochemical light source would be one in which each element in the electrode would be vaporized into the discharge, regardless of what other elements were present, at a fixed and unvarying rate, and in which the atoms of each element, once vaporized, would be excited to radiate a spectrum in which the spectral lines varied in intensity with concentration according to an invariable and definite law.

In all ordinary light sources, however, the relative intensities of the lines of any one element and of lines of different elements vary from instant to instant, for a variety of reasons. In electrical discharges, fluctuations in temperature, caused by current variation or ventilation changes, result in fluctuations in the relative intensities of lines with different excitation functions. The potential gradient in a discharge is affected by the ionization potential of the atoms present and so will depend on the kind and number of atoms present other than those under analysis. Further, the rate and order in which different elements evaporate from the electrodes into the discharge depends on the relative

vapor pressures and boiling points of the other elements present, as well as on local variations in electrode temperature.

While the effects of the worst fluctuations are eliminated by the "internal standard" method, experiment reveals wide variations in the errors introduced by the light source. It is therefore necessary to consider carefully the type of light source to be used and its best adjustment.

The flame, as a spectrochemical light source, has been strongly advocated by Lundegårdh. (See page 21.) His method, in which a solution is sprayed into an acetylene-air flame, is especially suitable for biological analyses—such as those of soil, plant, and animal samples—and for readily soluble inorganic material. Lundegårdh has applied it to 34 of the commoner metallic elements. The sensitivity is found to be from 0.001 to 0.000001 mol per liter for the various elements; and since high concentrations can be handled by simple dilution of the sample, the method is applicable to almost any initial concentration. Suitable reference elements are readily introduced into the solutions. The error is said to be never in excess of 5 per cent of the amount present and often not more than 1 or 2 per cent. This accuracy is as good as that secured with the best of other sources, but the method has not been widely adopted in this country—no doubt because of the somewhat greater convenience of arcs and sparks, for most types of sample.

As has been noted earlier (Sec. 12), the d-c arc, in spite of its simplicity and its high sensitivity in the detection of traces of impurities, is subject to erratic fluctuations that limit it to quantitative work in which only moderate precision is required. To a large extent, the difficulties are due (page 22) to the wandering of the cathode spot, with resultant variations not only in the temperature of the discharge but also in the location of the disengaging spot on the cathode and in the duration of disengagement from any one spot. Elements of low boiling point enter the discharge more rapidly and are depleted from the disengaging area more rapidly than elements of higher boiling points.[6] Fluctuations follow in both the relative and total number of different kinds of atoms entering the discharge. The arc then varies both in intrinsic brilliancy and in total intensity and volume, as well as in the relative distribution of intensity among the different spectral lines.

With these variations in the temperature, volume, and density of the discharge there is, of course, a related variation in the extent of absorption of the radiation from deeper within the discharge by the outer layers. By Kirchhoff's Law (page 8), the atoms of the outer layers absorb those wave lengths which they are themselves able to radiate. The result is a varying self-absorption, especially of the lines involving the

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[6] Richardson, *Proc. Fifth Conf. on Spec., 1937*, p. 64. New York: J. Wiley and Sons, 1938.

lower energy states of the atom, which produces a greater or less "self-reversal" of the lines. Except for the most strongly reversed lines, which may appear as two lines or wings with a more or less completely absorbed center, the effect of partial self-reversal is a variation in the apparent intensity of the lines affected. For light sources which do not operate at very low pressure, where absorption is small, varying self-reversal is a serious cause of fluctuations in the relative intensities of different lines in the spectrum.[7]

To some extent these variations will average out over the whole exposure. This averaging process can be furthered by including the results of two or more exposures. Actually, no amount of averaging can remove the difficulty entirely, since the relative and absolute intensity variations are not linear in the variables and often not even systematic. It is usually difficult to reduce the source errors below 10 per cent.

A better form of arc for quantitative work and one which is nearly, if not quite, as sensitive as the d-c arc is the a-c arc (page 22). It can be used in practically every problem to which the d-c arc is applicable, and, indeed, because of the lower resulting electrode temperature, with some electrode materials that would melt or burn at d-c arc electrode temperatures. For analyses in which high sensitivity is needed, as in trace analysis or the analysis of low concentrations of any kind, it is probably the most useful source. Originally developed by Duffendack and Thompson for the analysis of solutions, it has been adapted to sheet and cast-steel samples (Sawyer and Vincent), to aluminum and magnesium analysis at the Dow Chemical Company laboratories, and to many similar problems. In most applications the errors can, with care, be kept under 10 per cent and often to about 5 per cent of the amount determined.

Where greater accuracy is required without the highest sensitivity, some form of condensed spark source is almost essential. The actual sensitivity attainable by the spark depends on sample composition and form and on equipment, as well as on the spark characteristics, but it is probably always less than the sensitivity attainable by an arc with the same sample and apparatus. The range, however, is greater and, by a choice of two or three line-pairs to cover successive ranges, may often be from a few hundredths of a per cent to several per cent. The spark is thus better suited to composition analysis than to trace analysis or inspection—a field which is rapidly growing in the importance of its applications.

The simple condensed spark has been used in numerous spectrochemical installations. For certain types of samples, it has proved very satisfactory. The spark, like the arc, however, is subject to erratic

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[7] G. H. Dieke and H. M. Crosswhite, *J. Opt. Soc. Am.*, **33**, 425, 1943.

fluctuations. These fluctuations seem to be due largely to variation in the number of oscillating arc discharges in the train which follows each spark breakdown (page 24). In some cases, proper choice of the frequency of the spark circuit or the use of a de-ionizing air blast on the spark gap may give sufficient control over the spark.

In many cases of metallic analysis, particularly in the case of steel, adequate control is difficult to attain, and an auxiliary synchronous gap has proved very useful. In this circuit (Fig. 4, page 24), a synchronous gap permits the spark discharge to pass only for a brief interval at the peak of each voltage cycle, while an air blast on the sample gap helps damp the discharge train.

With a source of this type, the installation at the foundry of the Ford Motor Company, described by Vincent and Sawyer,[8] carries out rapid routine analyses of iron and steel, with a probable error in a single determination of the order of 1.5–2.0 per cent. Analysis is made for copper, chromium, manganese, molybdenum, nickel, and silicon, for percentages ranging from 0.1 to 0.2 per cent to 5 per cent or more. The ranges are limited by the demands of the problem; they could be extended by suitable choice of lines and exposure conditions. The errors, of course, arise only in part from source fluctuations; in fact, the source errors here are near their lower attainable limit. The source and distribution of the other errors will be discussed below.

The accuracy of results may be significantly affected by the size and shape of the electrodes. With the spark, for example, it is desirable to use a size and tip form such that the discharge will play over it in a uniform and regular manner. This effect may be attained by using one flat and one pointed electrode, or two electrodes with blunt, conical tips. The size of the electrodes and the angle of the cone are fixed largely by the power of the spark circuit. Larger electrodes are possible for more powerful outfits. For a large outfit drawing about 2.5 KVA in steel analysis, electrodes $\frac{3}{32}$ in. in diameter and with conical tips of 148° included angle have been used.

120. Selection of Spectrograph

Quantitative spectrochemical analysis may be carried out with any spectrograph of good design, with low scattered and reflected light, that affords sufficient dispersion to separate the spectral lines of the samples. It should be possible to attain the separation with a slit width of 20–50 microns, since the resulting line widths lead to smaller microphotometer errors. As large a dispersion as possible is also desirable in line spectrum work, since the continuous or unresolved band spectrum background is thereby diluted relative to the line spectrum, and thus background,

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[8] H. B. Vincent and R. A. Sawyer, *Metal Progress*, **36**, 35, 1939.

always troublesome in photometric work, is reduced. On the other hand, spectrographs of smaller dispersion are generally cheaper and faster and may be adequate for spectra which are not too complicated.

There is no one best type of spectrograph for all types of spectrochemical work. Quartz prism spectrographs have been frequently used because so many of the elements have their sensitive analysis lines in the ultraviolet regions. The sensitive lines of elements to the left and bottom of the periodic table, however, tend to be found in the longer wavelength regions, and glass spectrographs are, accordingly, more suitable for these elements, although they can be used with some success for nearly all elements. The use of grating spectrographs has been limited in the past by the lack of an adequate commercial supply of gratings. Recently, replica gratings of quality adequate for many problems have become available, and demand will doubtless stimulate production of more gratings. The simplicity of grating spectrographs, together with their large dispersion and resolving power in the visible region, should lead to their wider use.

121. Photographic Emulsion Requirements

In photographic emulsions, also, a wide variety has been used. The ideal material should have high contrast, to give satisfactory sensitivity to concentrational variation; small grain size and low chemical fog to reduce photometer errors; and uniform sensitivity and contrast over a wide spectral range to avoid the necessity of more than one calibration curve. Such emulsions are usually slow, but low speed is often desirable to permit long enough exposures for good sampling of the material. Contrast and process emulsions satisfactorily fill most of these requirements. The Eastman Spectrum Analysis No. 1 Emulsion developed especially for the spectrochemistry of metals combines most of the properties of contrast emulsions with rapid processing made possible by a thin, hard gelatine layer. This emulsion, however, does not have so long a region of uniform contrast as do some of the other emulsions. It must therefore be used with caution above 3400A or below 2400A.

Whatever the emulsion used, a significant source of experimental error is grain in the emulsion, which leads to variation in microphotometer readings in successive settings on the same line because of difference in the number of grains included. This uncertainty can be reduced by increasing, as much as possible, the area of spectral line photometered; the error, in fact, is inversely proportional to the square root of the area photometered. Sawyer and Vincent[9] have shown that by using a photometered area as large as 5 millimeters long and 50 microns wide,

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[9] R. A. Sawyer and H. B. Vincent, *J. Opt. Soc. Am.*, **31**, 47, 1941.

the mean error from this source may, under favorable conditions, be kept as low as 1 per cent.

Errors also arise from variations in emulsion sensitivity from point to point. Since these errors tend to increase with distance, it is highly desirable to have the reference pair of lines close together on the plate—within a millimeter or two if possible.

122. Photometric Procedure

Almost any of the methods for the photometric determination of line intensities described in Chapter 12 may be used in quantitative spectro-chemical analysis. Since the intensities, or relative intensities, of comparatively few lines in the spectrum are needed, a spotting or non-recording microphotometer is usually more convenient than a recording instrument.

It is desirable to photometer a considerable length of line, say from three to five millimeters. Such a length can hardly be attained with a rotating-sector method of line weakening. The errors resulting from this method, then, which has been widely used because of its simplicity, will generally not be so small as those from other methods, and, accordingly, it should not be used unless source and other errors make the photometer errors insignificant. Sawyer and Vincent[10] have pointed out that with most emulsions the reciprocity-law error introduced by the use of the sector is by no means negligible.

For plate calibration, spectral lines of known relative intensities or photometric marks of similar form should be used. Such procedure will reduce difficulties from Schwartzschild-Villiger effect in the micro-photometer, and from Eberhard effect in the emulsion.

It should be noted that, since only relative line intensities are required for the analytical curve (Fig. 107), it is not necessary to fix accurately the zero either of intensity or of galvanometer deflection (density). Only differences on these scales are used (see page 264).

123. Magnitude of Errors

The errors which enter into spectrochemical determinations have been discussed in detail by several authors.[11] With proper procedure, except in very unfavorable cases, the mean error of a single observation should not be over 10 per cent. Much work is done regularly with an error of only 5 per cent. With the best equipment and technique, stand-ard deviations have been reported as low as 1.1 per cent for antimony in

[10] R. A. Sawyer and H. B. Vincent, *J. Opt. Soc. Am.*, **33**, 247, 1943.

[11] H. Kaiser, *Zeits. f. Tech. Physik*, **17**, 227, 1936; Sawyer and Vincent, *J. Opt. Soc. Am.*, **31**, 47, 1941; **32**, 686, 1942; H. H. Grossman, R. A. Sawyer, and H. B. Vincent, *J. Opt. Soc. Am.*, **33**, 185, 1943.

lead[12] and 0.8 per cent for chromium in steel.[13]   Such results are obtained for favorable cases, of course, and for concentrations in the range from about 0.5 to 5.0 per cent.   For higher concentrations, the error is likely to be increased by the difficulty of finding analytical lines which are not so dense that they lack sensitivity; while for trace concentrations, there is apt to be difficulty in correcting the weak analytical line for plate background.   In most other cases, however, suitable analytical lines can be chosen for the desired range to give a straight analytical curve of satisfactory slope.

If the analytical lines are properly chosen, the various accidental errors which occur in spectrochemical analysis tend to have a constant percentage relationship to the quantity to be determined, regardless of its size.   On the other hand, the error in gravimetric chemical methods is rather a constant absolute error.   Accordingly, since the absolute spectrochemical error increases with content, the gravimetric method is relatively better at higher percentages, while the spectrographic method is likely to be better for low and trace analyses.   As a rough rule, it may be stated that, for the best practice with metallic electrodes, the accuracy of spectrographic analysis is better than that of chemical analysis for concentrations below about 0.5 per cent and approximately the same for those between 0.5 and 5.0 per cent; while for higher concentrations, chemical wet methods are likely to be more accurate unless special spectrographic techniques are used.

124. Speed of Analysis

As to the rapidity of the two procedures, much depends on the type of analysis.   Spectrochemical analysis is not so systematized as chemical.   That is, it is not possible to specify in advance a general procedure applicable to any or all equipment.   Each new kind of sample or element to be determined presents a problem calling for more or less investigation to fix exposure and source conditions, analytical line-pairs, and analytical curve.   Once these conditions have been determined, succeeding routine analyses can be carried out very expeditiously.   Owens[14] has reported results from a large industrial installation showing that the average time required for a determination is only seven man-minutes, while the chemical methods previously employed took at least four times as long.   Vincent and Sawyer[15] have described a large installation for iron and steel analysis in which a high-precision analysis of a sample for as many as six minor constituents can be completed and reported in six minutes, and

[12] H. Kaiser, *Zeits. f. Tech. Physik*, **17**, 227, 1936.
[13] H. B. Vincent and R. A. Sawyer, *J. Opt. Soc. Am.*, **32**, 686, 1942.
[14] J. S. Owens, *Ind. & Eng. Chem.*, **10**, 64, 1938.
[15] H. B. Vincent and R. A. Sawyer, *Metal Progress*, **36**, 35, 1939.

in which two shifts of four operators each handle over 300 samples in a 16-hour day.

125. Absorption Spectrophotometry

In addition to the increasing use of emission spectroscopy in the determination of the presence and concentration of the chemical elements, there is a wide use of absorption spectra for the detection and study of organic and inorganic compounds. As has been noted in Section 92, the general problem of qualitative analysis by band spectra through the identification of the molecules responsible for a band or band system is much more difficult than the corresponding line emission problem. The great number of possible compounds and the similarity of the absorption spectra of allied compounds are responsible for this difficulty.

Many instances, however, will be found in the literature showing that spectrophotometric measurements of the absorption of materials have yielded valuable information on their composition or purity. These measurements have been made in all parts of the spectrum, from the vacuum-ultraviolet to the extreme infrared. A few examples only can be mentioned. The measurement of the absorption of carbon dioxide[16] in the infrared has led to the development of an extremely sensitive and rapid method of determining the carbon dioxide content of the air, which has had important applications in the study of various types of respiration: human, animal, and cellular. Ultraviolet absorption measurements have for several years been used for the determination of vitamin A and for the standardization of fish-liver oil concentrates.[17] Many processes in organic and inorganic chemistry are regularly controlled and analyses made by spectrophotometric processes.

A discussion of these procedures in detail would require a more extended treatment of molecular theory and band spectroscopy than can be given here. In the following bibliography several references will be found to publications which discuss the applications of absorption spectroscopy, with extensive references to the literature.

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[16] E. D. McAlister, *J. General Physiology*, **22**, 613, 1939.

[17] Report of A. D. M. A. Vitamin Assay Committee, *J. Am. Pharm. Assoc.*, **26**, 525, 1938.

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